

Clarendon Press Series

EXERCISES
IN
PRACTICAL CHEMISTRY

BY

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AND

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LONGUM IN ER EST PER PRAECEPTA, BREVE ET EFFICAX PER EXEMPLA
Seneca, Lib. I Lp. VI

Fifth Edition

REVISED BY

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P R E F A C E

THE object of this volume is to furnish a systematic course of study to those who are beginning to learn Chemistry practically. The course commences with a series of exercises upon the preparation and properties of some of the most familiar substances, in which precise directions are given as to the apparatus and materials to be used, and as to the manner in which each experiment is to be made. In the earlier exercises, especially, the directions given extend to minute details; the aim of the authors being to provide, as far as possible, all the guidance that a beginner, working by himself or with only occasional supervision, may require. A few exercises have been introduced on parts of manipulation which, from their importance, it seemed desirable to treat separately; but, as a rule, each operation is described where the occasion for its use first arises: and the subjects have been so chosen as to furnish examples of all the usual chemical operations. The attempt has been made to arrange each exercise so as to provide the student with continuous occupation, and economise his time by giving two or three operations which can be carried on simultaneously and to which he should direct his attention in turn. The time required for the completion of different exercises cannot but vary considerably, since some operations, too important not to be included, do not admit of being hastened; but in most cases about two hours will be found sufficient.

The list of apparatus given at the outset shows what it is desirable that a student should have for the performance of the exercises; but those who have not access to a chemical laboratory, and who are unwilling to incur the expense of providing themselves with a complete set of apparatus from a chemical dealer, will find in the Appendix a number of suggestions for the construction of pieces of apparatus which can be made very cheaply.

The authors have endeavoured, by repeating nearly every experiment in exact conformity with their written description, to ensure that the student who carefully follows their directions shall command success; but as they cannot but fear that many errors and omissions may, nevertheless, have escaped them, they will be grateful for any suggestions from those engaged in teaching who may make use of their book. It is only by a large experience of the errors into which beginners are liable to fall that the many ways of going wrong can be discovered and stopped.

The question of chemical nomenclature is at present in such a condition that every lecturer or writer must choose for himself the names he considers least objectionable. The names assigned to substances in this volume are, with a few exceptions (made with a view to consistency), the same as are used in Roscoe's 'Lessons in Chemistry,' and Watts' edition of 'Fownes' Manual.'

The illustrations in the text have, with very few exceptions, been drawn directly on the wood from photographs, taken by one of the authors, of the apparatus actually used.

PREFACE TO THE THIRD EDITION

IN preparing the present edition, the Editor has, in the first place, to regret the loss of the co-operation of Mr. Harcourt, whose care, accuracy, and discrimination gave to the former editions a value which the present one cannot justly claim to possess.

Some more or less important alterations will be noticed in the present issue, chiefly of the following kinds—

1. The succession of the Exercises has been to a certain extent re-arranged, so as to make them follow more nearly in the order in which a beginner would probably study the radicles in the course of his reading.

2. A few additional Exercises, such as those on Weighing and Measuring, and on Chemical Action, and a rather large number of additional experiments have been introduced; such experiments alone being selected as can be made without much risk, and with the simplest apparatus¹.

3. Short headings have been placed before most of the experiments, in order that the student may appreciate more clearly what the experiment is intended to illustrate, before he performs it.

Practical Chemistry seems in danger of being made far too much a study of a few reactions of salts, got up for the purpose of detecting them in the course of an analysis. This is, of course, due to the requirements of examiners, to satisfy which

¹ Suggestions for an advanced course of experimental work, which requires experience and more elaborate apparatus, will find a more appropriate place in the second volume.

nearly all the very moderate time available for practical instruction in schools must at the present day be spent. Moreover analytical work (in the narrow, technical sense) entails, like Latin verses, less trouble to the teacher and less risk to the pupil than other kinds of practical work; while it undoubtedly affords, when intelligently pursued, a very excellent training in the application of logical methods.

But it may well be doubted whether a more real and valuable advance in a scientific education is not made by the careful preparation and examination of the properties of such a substance as oxygen, or by an exact study of a few examples of oxidation and reduction, than by simply observing, for instance, that chlorides give a white precipitate with silver nitrate which is soluble in ammonia.

It is hoped that this book may do something towards tracing, for those at any rate who have time and enthusiasm for the work, an outline of a rather wider range of study.

H. G. MADAN.

ETON, *September*, 1880.

PREFACE TO THE FOURTH EDITION

IN the present edition some verbal alterations have been made, some additional experiments and one or two additional Exercises (such as the one on Combustion and Flame) have been introduced, and the course of analysis of a single substance has been somewhat altered; with, it is hoped, a gain in clearness and completeness.

In many cases, especially in dealing with the metals, the preparation of useful compounds of the radicle has been

more fully treated of, instead of merely alluding to them incidentally in the course of analytical reactions. Beginners are too often inclined to attach an almost superstitious value to the mere formation of a 'Precipitate'; as though, having once 'got' it, they need think nothing further about the reaction; whereas both the insoluble product and the substances remaining in solution may be not only of theoretical importance but of practical utility.

H. G. MADAN.

ETON, May, 1887.

PREFACE TO THE FIFTH EDITION

SCARCELY any changes beyond a few verbal alterations and a few additional woodcuts have been thought necessary in preparing the fifth edition.

While Chemistry in its higher branches has undergone a vast development, both as regards theory and also in experimental methods, during the quarter of a century which has elapsed since the first edition of these Exercises appeared, the requirements of the beginner remain the same. He still needs that careful training in accuracy of observation, neatness in manipulation, and sound acquaintance with the elementary facts of the science, which it was the original object of this book to afford, and which, it is hoped, may still be found in its pages.

H. G. MADAN.

OXFORD, November, 1896.

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Memoranda

1. BE orderly and neat in manipulation. Cleanliness stands at the head of the chemist's scale of virtues. All messes must be cleared away with the zeal of a sanitary inspector.

Never go to work, or continue to work, with the table covered with a litter of bottles, flasks, basins, and test-tubes; but replace each bottle on its shelf as soon as you have done with it, and have a basket or basin at hand into which to put dirty test-tubes, &c.

Always wash your test-tubes twice: once, before they are put away; and again, with distilled water, immediately before they are used. Probably more puzzling reactions occur from the use of dirty test-tubes than from any other cause.

2. Do not begin work in a hurry. What is expended in time is very often gained in power, in grasp of a subject. Yet, on the other hand, learn to be economical of time. Several filtrations and evaporations, for instance, may be going on at once. The chemist may, sometimes, in spite of the proverb, do more than one thing at a time, by allowing things to do themselves.

3. Be economical of materials. In analysing a substance, do not (without the strongest reasons) use up at once the whole quantity at your disposal. Reserve at least one-fourth of it in a corked tube or covered watch-glass, in case unforeseen accidents should occur and the other portion should be lost. In making a gas, the residue left in the generating vessel will often be of use, at any rate interesting as a specimen. It should not, as a rule, be thrown away, but purified by recrystallisation or otherwise.

4. Never begin an experiment until you have looked over all the preparations for it, to make sure that you have everything that is necessary within reach. You will not then have the mortification of seeing the half-performed experiment fail for want of some requisite which cannot be procured at the moment.

5. Do not think merely of what will *do*, but what is *best*, of the means at your disposal. Whatever is worth doing at all is worth doing thoroughly well.

6. Never add one chemical substance to another without considering for what purpose you add it, and what various effects may be produced.

7. Be exact and methodical. Let nothing pass unnoticed, although you may not see its significance at the moment. Make written notes of everything that you do, analyses of lectures, sketches of apparatus. Whatever is worth doing is worth recording.

8. Do not attempt to devise a modification of an experiment until you have tried it in exact accordance with the directions given. Then, and then only, if you fail, you will find it possible to blame the book and not yourself.

9. Do not expose yourself needlessly to vapours which you know to be injurious, e.g. chlorine, hydrogen sulphide, hydrogen arsenide. Remember that the bad effects may not be perceptible immediately.

10. Finally, do not look upon Chemistry as a mere amusement, as a means of getting up a few explosions, creating a few unsavoury smells, producing a few striking changes of colour. Chemistry is worthy of better treatment: it is no longer a 'black art,' but a refined science, and should be thoughtfully and reverently studied.

Nor, again, give up hopes of making discoveries in the science because the land appears to be already highly farmed, and you have not all the refined apparatus which the optician and operative chemist can supply. Records of close and accurate observations of some of the (apparently) simplest phenomena of Chemistry are much needed; and such it is in the power of every student to contribute.

Ad Chemicum.

Narem illaudatis vehementer odoribus angis,

Aurem terrifico percutis usque sono.

Quippe oculum, Chemeia, magistra haud alma, vel ipsum

Corripis, et digitos inane petisque caput.

Quid manet? una fides manet inviolata tuorum

Semper, et ut crescant vulnere crescit amor.

H. G. M.

LIST OF APPARATUS

*Required for the Course of Practical Work contained in
this Volume¹.*

[The abbreviation cm. stands for centimetre.

„ „ mm. „ millimetre.

„ „ c.c. „ cubic centimetre.

„ „ grm. „ gramme.

For tables of weights and measures see Appendix E.]

1. A Common Metre (or Half-metre) Rule; the first decimetre divided into millimetres, the rest into centimetres.

2. A Cylindrical Graduated Glass measure, to contain 200 c.c.; graduated into spaces of 5 c.c.

3. A Pair of Scales, with beam about 20 or 25 cm. long, sensitive to a weight of 1 centigramme². The ordinary grocers' scales, if well made, are sufficiently good. Such a balance is shown (arranged for use in a Bunsen's holder) in fig. 46, p. 47.

4. A Set of Weights, from 100 grms. to 5 centigrammes (or, better, 1 centigramme). These need not be of the highest accuracy: such sets, including 100, 50, 20, 10, 10, 5, 2, 2, 1, .5, .2, .2, .1 grm., mounted on a wooden stand, are sold in France for a price equivalent to less than half-a-crown, and can be procured in England at

¹ In making this List it has been thought right to err rather on the side of completeness than of deficiency. Some pieces of apparatus, e.g. a Bunsen's holder, are not absolutely necessary; and in several cases the student will be able, by the aid of a few tools and a little ingenuity, to make substitutes for himself. Some suggestions for the construction of economical apparatus will be found at the end of the book (Appendix A), but no direct reference to such substitutes is made in the text, since the student, who is ingenious enough to make a piece of apparatus for himself, will be at no loss to bring it in where it is wanted. If supplies have to come from a distance, at least twice the number of such things as flasks, test-tubes, watch glasses, should be obtained.

² For supporting the scale-pans, brass wire stirrups are far preferable to chains or cords; but common balances are seldom fitted with them. The wire frames shown on p. 52 obviate some of the inconveniences of chains, and should be fitted at once, if the balance has chains.

a reasonable cost. Such a set of weights is shown in fig. 46, ¹ 47, near the balance on the right-hand side. The smaller weights, decigrammes and centigrammes, can easily be made (or replaced, if lost) by the method given in Appendix A.

5. A Pneumatic Trough, about 36 cm. long, 24 cm. wide, and 16 cm. deep, fig. 1. This is an apparatus for collecting and experimenting upon gases, and consists of a cistern for holding water or any other fluid, furnished with a movable shelf placed across it

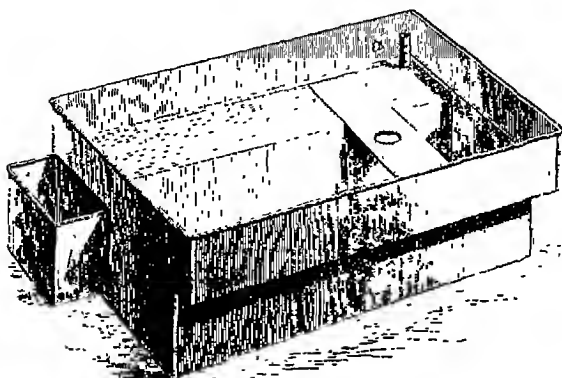


Fig. 1.

about 5 or 6 cm. below the top. In the centre of the shelf is a hole, which should not be less than 2 cm. in diameter, and immediately underneath this hole is soldered a broad, very shallow funnel, the mouth of which is of the same width as the shelf: the accompany-



ing figure represents a section of the shelf at this point¹. This funnel serves to catch bubbles of

gas, in case the delivery tube is not exactly under the centre of the hole, and to direct them upwards through the hole into a jar placed above it. In addition to these essentials, the trough represented in the figure has a ledge running along the whole length of one side on which jars may stand when filled with gas, and also an overflow-pipe *a* at one corner, the mouth of which is about 3 cm.

¹ A long narrow opening, extending nearly the whole length of that part of the shelf which is unsupported, is more convenient than a round hole. Its width need not exceed 7 cm., and on each side of it should be a strip of metal, soldered slanting to the under surface of the shelf, serving to strengthen the shelf and to guide bubbles of gas to the opening. The figure above represents a cross section of this part of the shelf.

above the level of the shelf, to convey any excess of water into the supplementary trough, *b*. These troughs are made of japanned tin, and it is a decided advantage to have the inside japanned white, as a much better view of the position of tubes, jars, &c., when immersed in the water, is thus obtained. For the method of using the pneumatic trough, see p. 105.

6. A Retort Stand, fig. 2, with rectangular iron foot, iron rod

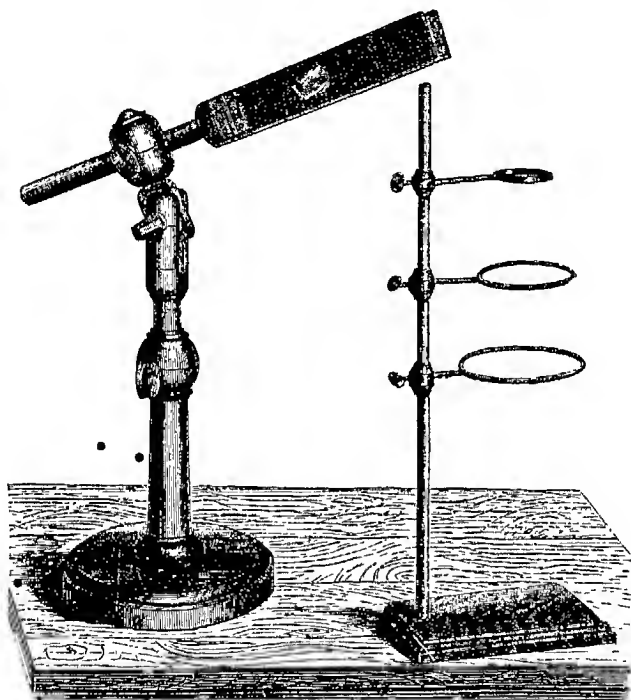


Fig. 3.

Fig. 2.

about 36 cm. in height, and three brass (or, preferably, iron) rings.

7. A Bunsen's Universal Holder, fig. 3, of stained beechwood, the smaller of the two sizes which are sold. This, although rather expensive (about 5*s.*), will be found a most useful piece of apparatus, both for chemical and physical experiments. Its construction will be sufficiently evident from the engraving. A notch should be cut across the cork near the end of each jaw, to hold round things, such

as test-tubes, more firmly. If the screws work stiffly, a little black-lead, in preference to tallow, should be applied to them.

8. A Bunsen's Burner, fig. 4, small size.

This burner consists of a brass tube, about 1 cm. diameter, having several holes close to its lower end, which, in the best form

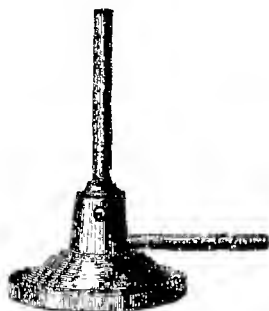


Fig. 4.

of burner, can be closed when desired by a revolving cap. Gas is introduced through a small flattened central jet, the orifice of which is just above the holes. Thus the gas is allowed to mix freely with air which enters through the holes; the supply of air being increased by the upward rush of the gas, in the same way as the draught in the chimney of a locomotive is increased by the blast of escaping steam.

In order to understand the principle of this most useful burner, the character of the ordinary gas-flame should be first studied. Close the air-holes by turning the cap (or with the fingers), turn on the gas, and light it at the top of the tube. It will burn with the usual bright white flame of coal-gas. The reason of its brightness is this:—Coal-gas consists mainly of hydrogen and compounds of hydrogen with carbon. Both these elements unite with oxygen, producing heat in doing so: but oxygen has more affinity for hydrogen than it has for carbon, and hence, when insufficient air is supplied, the oxygen in it combines with all the hydrogen, but with only part of the carbon. The rest of the carbon is separated in the flame, and its particles heated to whiteness give the brilliancy to the flame. The presence of these particles of unconsumed carbon in the flame may be proved by holding a white plate in it for a moment; the particles are thus cooled down and deposited as soot.

Now open the air-holes, and observe that the brilliancy of the flame vanishes entirely, though its size remains about the same. It is now of a faint bluish colour, steadier, and with better defined edges. The reason is this:—By the admission of air through the holes so much oxygen is mixed with the gas before it arrives at the top of the tube where it is kindled, that, together with the supply obtained from the air surrounding the flame, there is enough to com-

bine with all the carbon as well as the hydrogen of the gas. Thus none of the carbon is separated in a solid form, and the flame loses its brightness but gains in temperature, owing to the immediate and almost complete combustion which takes place: increase in the amount of chemical combination producing, of course, increased heat.

The absence of carbon particles may be proved by holding in the flame a white plate; no soot at all will be deposited, but only drops of condensed water-vapour.

The temperature of the flame may be tested by holding in it, near the top, a piece of moderately thin copper wire: the end will soon become bright red-hot and melt. It will be found impossible to melt a thin iron wire or piece of platinum foil in the same way¹.

One or two precautions should be observed in using this burner.

1. The supply of air must not be too great.

If much more than half the total volume of air required to burn the gas completely, is admitted through the holes, the mixture becomes too explosive, and the flame passes down the tube, continuing to burn at the jet below, with a small smoky flame, the heat of which is mainly expended on the tube itself. In such a case, the gas must be entirely turned off, and kindled afresh. If the flame is still unsteady and shows a tendency to recede down the tube, owing to a low pressure of gas in the main, the air-holes should be partially closed by turning the cap (or, if there is no cap, by plugging up one or more of them with bits of cork).

In fact, it is always best to cut off the supply of air altogether before lighting the burner, and then to admit just sufficient air to destroy the luminosity of the flame. In this way even a small flame, 2 or 3 cm. high, can be safely obtained.

2. The supply of gas must not be too great, and it must be thoroughly mixed with the air before reaching the top of the tube. This latter condition is effected by the peculiar shape of the jet. If the flame is white even though the full supply of air is admitted through the holes, the gas should be partly turned off. If the flame still shows luminosity, there is reason to suspect that the jet is out of order, or that the air-holes are clogged by dust or some fused substance which has dropped down the tube. The main tube should be unscrewed and the jet and air-holes examined and cleaned.

¹ The actual temperature of the flame is estimated at more than 2000°, but unless it is enclosed in a furnace, a large amount is lost by radiation.

3. The hottest part of the flame is a little below the top and near the border. This can be proved by holding a piece of platinum foil in various parts of the flame and observing where it glows most brightly.

4. The interior of the flame has a strong 'reducing' action (*i. e.* it tends to withdraw oxygen from substances placed in it. This should be borne in mind when dealing with glass containing lead, which will be blackened, owing to the separation of lead, if held in the middle of the flame.



Fig. 5.

The cast-iron cap (or 'rose top') shown in fig. 5, when placed upon the burner, divides the single flame into a ring of small jets which distribute the heat over a large surface, and are well adapted for heating an evaporating basin or sand-bath.

9. A Cast-iron Stand, fig. 6, with screw, on which may be fitted the Argand burner *a*, the blowpipe jet *b*, and the fish-tail burner *c*.

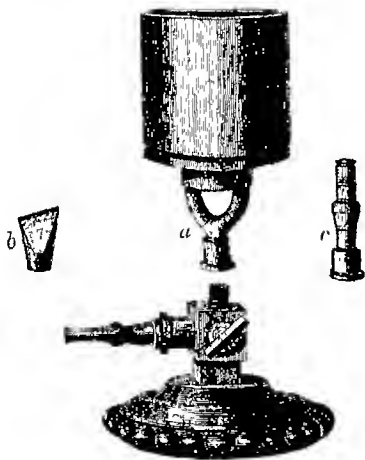


Fig. 6.

The Argand burner consists of a hollow ring or short cylinder of metal (or, better, of porcelain) pierced with a number of small holes through which the gas issues, giving a continuous circular flame, which is steadied by the short brass chimney shown in the figure. It is not absolutely required, but is extremely convenient for applying a gentle heat to a flask or sand-bath, since it is more under control than the Bunsen's burner and can be regulated to give the least possible flame.

The blowpipe jet is described in the Exercise on the use of the Blowpipe, p. 93.

The fish-tail burner, which is a common form of illuminating burner, gives a flat flame, very suitable for bending glass tubes.

10. A Set of Four Wooden Blocks, about 12 cm. square, and respectively 2, 5, 7, 10 cm. in thickness.

LIST OF APPARATUS.

11. A Test-tube Stand, of the usual form, for supporting test-tubes while in use. It should have twelve holes in one row, and a strip of slate should be fitted in front of the holes, on which may be written the contents of each test-tube when it is placed in the stand.

12. A small Dish, of tinned iron or copper, about 12 cm. in diameter, for use as a sand-bath.

13. Two pieces of fine Iron Wire Gauze, about 12 cm. square, to place under flasks, &c., while being heated. The gauze should have about 12-14 meshes in 1 cm. (30-36 meshes per inch).

14. A Mouth Blowpipe, fig. 7, about 20 cm. in length.



Fig. 7.

15. A small Ladle, with bowl about 7 or 8 cm. in diameter, and an Iron Spoon, or Capsule, fig. 8, about 4 or 5 cm. in diameter, for ignitions.



Fig. 8.

16. A Pair of Crucible Tongs, fig. 9, about 20 cm. in length.



Fig. 9.

17. A Set of four Cork-borers, fig. 10, from 3 mm. in diameter upwards. These are short pieces of thin brass tube, sharpened at



Fig. 10.

one end, and having a thick collar soldered to the other end, to afford a better hold. For the method of using them, see p. 37.

[When the cutting edge becomes blunt or bent, it should be sharpened on a hone, or by a very fine file, the borer being constantly rotated while the hone or file is passing over it.]

18. A piece of **Platinum Foil**, about 2 cm. \times 5 cm. It should weigh about 0.4 gram. This is used chiefly as a support for substances on which we wish to try the effect of a high temperature, in order to test their fusibility, volatility, &c. If the edges of the foil are turned up round a spherical mould, such as the end of a pestle, the foil being laid on the palm of the hand, and the pestle pressed forcibly upon it, we obtain a very convenient capsule for fusions on a small scale, *e.g.* for the decomposition of barium sulphate by sodium carbonate.

It should, however, be a rule—1st. Never to use a platinum vessel when a piece of porcelain or an iron spoon will do as well. A bit

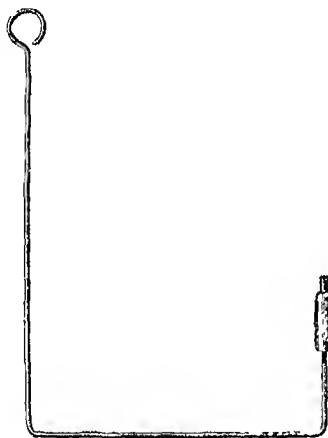


Fig. 11.



Fig. 12.

of a broken evaporating dish will serve for almost every purpose, except when silicon, aluminium, or the alkali metals are to be tested for.

2nd. Never to heat in a platinum vessel the following substances:—

Substances evolving chlorine or sulphur.

Caustic alkalies or barium hydrate.

Cyanides, chlorates, nitrates.


Easily reducible metallic salts, or their corresponding metals, *e.g.* lead, silver, tin.

[When a platinum vessel is dirty, try first to clean it by boiling it in a dish with a little strong hydrogen chloride. If this has no effect, spread over the surface some powdered potassium-hydrogen sulphate, and heat

it over a Bunsen's burner until the salt fuses, inclining the vessel so that the liquid salt may flow over every part of it. Finally, boil it with water in a dish.

When a piece of platinum foil becomes creased or wrinkled, place it between folds of glazed writing-paper on a smooth surface, such as a plate of glass, and pass over it with strong pressure a rounded burnisher, such as the handle of a paper-knife, or the finger-nail.]

19. A piece of Platinum Wire, about 30 cm. long and 0.5 mm. in diameter (No. 25 standard wire-gauge). This is chiefly for use in blowpipe experiments.

20. Two pieces of Brass or Copper Wire, about 30 cm. long, and 1.2 mm. in diameter (No. 18 standard wire-gauge). These should be filed to a point at one end and then bent, the one into the form of fig. 11 (p. 8), the other into the form of fig. 12, and finally a small piece of wax taper about 3 cm. in length should be stuck upon the pointed end of each. One wire may be made to serve the purpose of the two pieces, if bent into this shape  and a piece of wax taper stuck on each end.

21. A Deflagrating Cup, see fig. 13. This consists of a brass or iron bowl about 1.5 cm. in diameter, screwed to a piece of stout iron wire which passes rather stiffly through a cork stuffing-box attached to a tin flange. It is intended to hold substances which are to be burnt in gases.

22. A Deflagrating Jar, fig. 13. This is a wide-mouthed stoppered jar, open at the bottom, about 22 cm. in height and 12 cm. in diameter. The top should be ground flat, in order that it may be accurately closed by a glass plate.



Fig 13.

23. Two strong cylindrical Glass Jars, for collecting gases (fig. 14), 10 cm. in height, 3 cm. in external diameter, with ground mouths. They should be made of thick glass, since they are used for holding mixtures of hydrogen and oxygen gases which are to be exploded.

24. Three similar Jars, which may be of thinner glass, 20 cm. in height, 5 cm. in diameter.

25. Two circular Glass Discs, 5 or 6 cm. in diameter, ground on one side.

26. One shallow circular Stoneware Tray, for holding gas jars, 8 cm. in diameter.

27. One Ditto, 18 cm. in diameter (see fig. 13). This, though convenient, is not necessary, as a common dinner-plate may be substituted for it.



Fig. 14.



Fig. 15.

28. Four Florence Flasks, fig. 15. These may be procured from any oilman, and should be selected of uniform thickness, free from air-bubbles, and with even mouths not chipped away at one side. The mouths of these flasks should be 'bordered,' *i.e.* turned outwards so as to form a spreading rim. Directions for doing this are given on p. 44.

[In order to cleanse them, put a few lumps of common 'washing soda' into each, add a little water, and heat it gently over a lamp, turning it round so as to bring the salt into contact with every part; finally, rinse it thoroughly, first with common water and then with distilled water, and place it to drain mouth downwards in the ring of a retort-stand.]

29. Two Flasks with flat bottoms, fig. 16, holding respectively 200 c.c. and 250 c.c.¹ A rather larger flask, holding about 400 c.c., is occasionally useful.



Fig. 16.

30. One plain Retort, holding about 200 c.c.

31. One Stoppered Ditto, of the same size (see fig. 79, p. 157).

32. Two wide-mouthed Stoppered Bottles, of white glass, holding about 700 c.c., for use in experiments on gases.

33. Six Ditto, holding about 150 or 200 c.c.²

34. Two common corked Bottles, with moderately wide

¹ It will be well to have two or three more of these, at any rate of the 250 c.c. size, in case of breakage.

² It is a great advantage to have the stoppers of these gas bottles made much more conical than usual. They are then far less liable to become fixed in their places if the volume of gas in the bottle should contract.

mouths, holding about 200 c.c., for use as washing bottles, for gases.

35. Two Ditto, holding about 300 c.c., for containing water which is to be saturated with a gas, such as chlorine, sulphur dioxide, or hydrogen sulphide.

36. One Washing Bottle with tubes (fig. 17), holding 600 c.c. This is of great use for washing precipitates on a filter, and also for containing a supply of distilled water for general purposes in analysis. Its construction is sufficiently plain from the engraving, and directions for fitting the tubes, and the method of using the bottle, are given on p. 35.



Fig. 17.

37. Two Thistle Funnels, fig. 18, about 32 cm. in length.

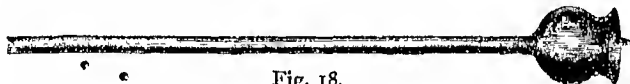


Fig. 18.

38. A Pipette, fig. 19, for transferring small quantities of liquid. It consists of a tube drawn out at one end into a jet, and slightly



Fig. 19.

contracted at the other end, so as to be readily closed by the finger. Directions for making one, and the method of using it, will be found on p. 32.

39. Three Glass Funnels, respectively 4 cm., 7 cm., 10 cm. in diameter.

40. Three Glass Beakers, respectively 4 cm., 5 cm., 6 cm. in diameter.

41. Twenty-four Test Tubes, of the following sizes:—

Eight	13 cm. in length,	1 cm. in diameter.	°
Fourteen	16 cm.	1.5 cm.	°
Two	20 cm.	2.5 cm.	°

One test-tube of the largest size, and about 8 or 10 of the smaller sizes should be kept ready for use, mouths downward, in a small wicker basket, No. 77.

42. Six Watch Glasses, 5 cm. in diameter.

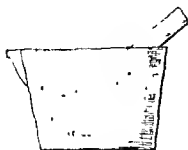


Fig. 20.

43. One Glass Spirit Lamp, in case gas is not available.

44. One Glass Mortar, 6 cm. in diameter, with pestle.

45. One Porcelain Mortar, fig. 20, 10 cm. in diameter, with pestle¹.

46. Two Porcelain Evaporating Basins, fig. 21, respectively 6 cm. and 9 cm. in diameter². A rather larger basin, 12 cm. diameter, is occasionally useful.

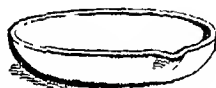


Fig. 21.



Fig. 22.

47. One Porcelain Crucible, with cover, fig. 22, about 3 cm. in diameter.

48. Two Drying Tubes, fig. 23, about 18 cm. in length. This

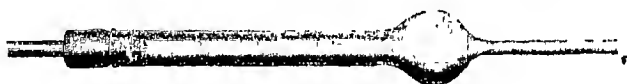


Fig. 23.

form of tube is intended to contain quicklime, calcium chloride, or other hygroscopic substance, in small fragments, for the purpose of removing moisture from gases which are passed through the tube. It is filled in the following way. After removal of the cork, a small tuft of cotton-wool or tow is pushed down into the bulb by means of a glass rod, until it lies across and protects the opening of the

¹ This mortar should not be glazed inside.

² These should be thin in substance (that there may be less risk of their cracking when heated over a lamp), and highly glazed both inside and outside. The Meissen ware is much the best, both as to shape and quality.


narrow tube. The rest of the bulb and the wide tube is then nearly filled with fragments of quicklime, or thoroughly dry calcium chloride, about as large as split peas. Another piece of cotton-wool is then lightly pushed in, to keep the substance in its place, and finally the cork with its short tube is replaced. It is advisable, when the tube is not in use, to keep the ends stopped by little plugs of cork, in order that the moisture of the air may not find entrance.

The calcium chloride for these tubes should not be fused, but only thoroughly dried at a temperature of 200° – 300° on a sand-bath. It is in this condition much more porous, and exposes a larger surface to the gas than the fused substance.

49. Twelve 'Ignition Tubes,' fig. 24, about 6 cm. in length. For directions for making such tubes, see p. 41.



Fig. 24.

50. Two kilogrammes of readily fusible Glass Tubing, free from lead, of different sizes, but chiefly about 6 or 8 mm. in external diameter¹,  (actual sizes).

51. Half a kilogramme of difficultly fusible Glass Tubing, 5 mm. in internal diameter (the larger of the two sizes shown above), for making 'ignition tubes' (No. 49) and arsenic tubes.

52. Two or three pieces of Combustion Tubing, about 30 or 35 cm. in length, and 12 or 14 mm. in external diameter.

53. Three or four pieces of Glass Rod, free from lead, about 50 cm. in length, and 4 or 5 mm. in diameter: for stirring-rods.

54. A piece of vulcanized India-rubber Tubing², about 1 metre in length, and 4 mm. in internal diameter: chiefly for use in connecting glass tubes; for which purpose pieces about 2 or 3 cm. in length may be cut from it, as required.

¹ The French soda glass is usually very good; but some specimens show a great tendency to devitrify when heated.

² Tubing of non-vulcanized india-rubber, which is also manufactured, adheres more closely to glass than the vulcanized tubing, and is in many respects preferable to the latter. It has the disadvantage of losing its elasticity in cold weather, but after being warmed and stretched a little, it regains all its good qualities. The red tubing, which is vulcanized with antimony sulphide, is slightly preferable to the ordinary gray kind.

55. Two or three pieces of similar Tubing, about 60 or 70 cm. in length, and 6 mm. in internal diameter: chiefly for connecting lamps with the gas supply. Also, 5 or 6 india-rubber rings, about 2.5 or 3 cm. in external diameter.

56. Two packets of circular Filters, respectively 7 cm. and 14 cm. in diameter, suited to the two smaller funnels (No. 39).

57. One box of Test Papers, containing books of blue litmus, reddened litmus, and turmeric paper.

[Blue litmus is turned red by acids,

Reddened litmus is turned blue by alkalis,

Turmeric is turned brownish red by alkalis.

Their use may be illustrated by laying strips of each side by side on a white plate, and putting on them a drop of (1) dilute hydrogen sulphate (sulphuric acid), (2) solution of potassium hydrate (caustic potash).]

58. Two brushes for cleaning tubes, fig. 25, one about 3 cm. in diameter, for test-tubes; the other about 5 mm. in diameter, for smaller tubes.



Fig. 25.

59. A 'three-square' (triangular) File, about 12 cm. in length.

60. A round (or 'rat-tail') File, about 20 cm. in length. These files should be fitted into handles.

61. A Spatula, about 8 cm. in length, broader at one end than the other, fig. 26. One made of platinum will cost 8s. or 10s., and will

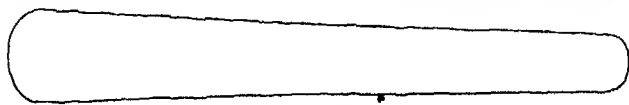


Fig. 26.

be found most useful. Instead of it, an aluminium or bone spatula of the same size may be obtained at a much lower price, and will answer for most purposes.

62. A few pieces of Charcoal, for blowpipe experiments. These may generally be selected from the ordinary rough beechwood charcoal. Sticks about 3 cm. in diameter, free from knots, should be picked out and sawn across the grain into pieces about 3 cm. in

length, or rather less (fig. 68, p. 102). When thus cut they should show a surface free from cracks and of close, sound texture.

63. A few bits of German tinder, and some spills. The thin, flat slips of cedar or pine are preferable, as they retain a glowing end longest. Instead of German tinder the ordinary cigar lighters, made of strips of pasteboard soaked in strong solution of saltpetre, or of loose cord impregnated with lead chromate, will answer well.

64. A common China Jug, holding about 2 litres.

65. Half a quire of White Blotting-paper, two or three quires of glazed writing-paper, and a few cards.

66. Two or three dozen good Corks of various sizes, from 1 to 6 cm. in diameter. Those should be selected which are free from fissures and cavities, and in which the grain runs *across* not *along* the cone.

67. Two or three Dusters.

68. Some clean, finely-sifted Sand, for use in the sand-bath and other purposes.

69. Five or six metres of Brass Wire, and also of copper wire, of the sizes No. 18 and No. 24, standard wire-gauge (about 1.2 mm. and 0.5 mm. in diameter, respectively).

The following pieces of apparatus are also extremely useful, and access to most of them will be assumed in the exercises:—

70. A Herapath's Gas Blowpipe, provided with a pair of double bellows, or with one of the small French india-rubber blowing machines, fig. 27 (next page). In this form of blowpipe the gas issues from a brass tube about 1 cm. in diameter, in the axis of which a smaller tube is permanently fixed, through which a blast of air is directed into the centre of the gas-flame. By attaching a larger or smaller nozzle to the air-tube and altering the quantity of gas, any kind of flame may be obtained, from a large brush-like flame 16 or 18 cm. in length, to a small pointed cone of flame, such as is required for analytical experiments.

The india-rubber blowing machine alluded to, consists of two parts: 1st, The blower, *a*,—an egg-shaped vessel of strong vulcanized india-rubber, having a valve fitted at each end enclosed in a small wooden box; 2nd, The regulator, *b*,—a spherical vessel of thinner india-rubber, with two necks, one of which is connected by an india-rubber tube with the valve-box at one end of the blower, while the other neck is similarly connected with the blowpipe air-jet.

When the blower is placed on the floor and compressed with the foot, the valve at one end closes, and the air contained in the vessel is forced through the other valve into the regulator, which becomes distended and forces the air through the blowpipe-jet. When the blower is relieved from the pressure of the foot, it recovers its shape, the valve nearest the regulator closes and prevents the return of the air, while a fresh supply of air enters through the other valve. When full, the blower is again compressed with the foot so as to force another supply of air into the regulator.

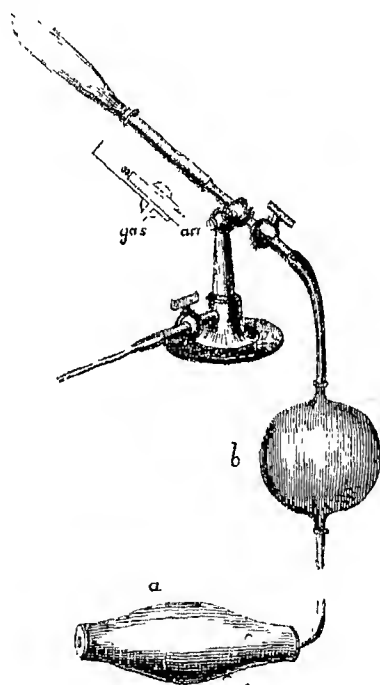


Fig. 27.

This blowing machine is much cheaper and more portable than any form of double bellows, and is very effective. The regulator is usually made too small, and thus there is a slight variation in the strength of the blast. The india-rubber must be of the best quality; and it is advisable to enclose the regulator in a net, to prevent its becoming so far distended as to burst.

Fletcher's blower, and a substitute which can be made without much difficulty, will be found described in Appendix A.

Although such a blowpipe as that which has just been described is necessary for some operations in glass blowing, and renders the chemist almost independent of a furnace for fusions on a small scale, yet much may be done by the use of the mouth blowpipe supported in a Bunsen's holder (so that both hands may be free) and directed upon a larger gas-jet than usual.

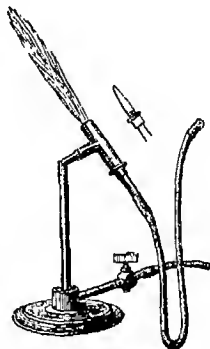


Fig. 28.

A very convenient form of Herapath's blowpipe is now made, which can be fitted on a Bunsen's burner, as shown in fig. 28. The air-tube is connected with a piece of india-rubber tube ending in a mouthpiece. No bellows are required, as sufficient air can be supplied by the mouth.

71. **A Platinum Capsule:** hemispherical, about 3 cm. in diameter. This, which would cost about 8s., will answer almost every purpose of a platinum crucible.

72. **A Thermometer,** with cylindrical bulb, fig. 29, graduated on the stem from -10° to $+150^{\circ}$ centigrade.



Fig. 29.

73. **A Writing Diamond:** a small splinter of diamond set in a brass holder, like a pencil.

74. **A light hammer,** of the form known as riveting-hammer.

75. **A small Anvil,** about 6 cm. square, and 2 cm. in thickness.

76. **A pair of cutting Pliers.**

77. **A small round Wicker Basket,** with upright sides, about 14 cm. in diameter and 10 cm. in depth; for holding test-tubes.

78. **A few sheets or cut filters of Swedish Filtering Paper,** for separating precipitates, such as barium sulphate or calcium oxalate, which from their finely-divided condition would pass through the pores of ordinary filtering paper.

A number of bottles will also be required for containing substances both solid and in solution. Many substances, such as

calcium chloride, from their alterability in the air, will of necessity be purchased in bottles. Exclusive of these, the following stock of bottles will be probably sufficient¹ :—

24	wide-mouthed bottles,	with corks,	300 c.c. capacity.
24	"	"	100 c.c.
6	"	with glass stoppers,	300 c.c.
12	"	"	100 c.c.
12	narrow-mouthed bottles,	"	200 c.c.
30	"	"	100 c.c.
3	"	"	2000 c.c.

The common green or blue glass bottles, costing (when stoppered, from 3s. to 6s. a dozen, will answer quite as well as the more expensive bottles of white glass.

[When a stopper is found to be fixed immovably in the bottle, try to loosen it by tapping it, first on one side and then on the other, with a piece of wood such as the handle of a file, pressing the thumb against the opposite side of the stopper and taking care to direct the blows obliquely upwards, rather than directly across the stopper. If this does not succeed, heat the neck of the bottle by passing it to and fro over the flame of a spirit lamp, turning it constantly round. The neck will expand with the heat before the stopper, and if the latter is now tapped again, it will almost certainly be loosened. There is, of course, a risk of cracking the bottle if it is heated too suddenly, but as the success of the method depends upon the difference in temperature between the neck and the stopper, the heat should be applied quickly, and only for a short time. If this method fails put a drop of oil or glycerine round the stopper, and leave the bottle for some time in a warm room. The oil will work its way between the neck and the stopper, and the latter may generally be loosened by tapping. If the bottle contains potassium hydrate, a drop of hydrogen sulphate may be substituted for the oil, and will remove the alkaline cement.]

¹ It is not absolutely necessary for the beginner to start with so large a stock of bottles. Some substances, *e.g.* marble, sulphur, manganese dioxide, &c., may be kept in boxes. But bottles are far preferable, on the score both of cleanliness and security.

LIST OF SUBSTANCES

*Required for the Course of Practical Work contained in
this Volume¹.*

THE numbers in the column on the extreme left of the page are intended to give some idea of the relative quantities of the substances which will be necessary. If 1 be interpreted to mean 10 grammes (about one-third of an ounce), 2=20 grammes, 3=30 grammes (about 1 oz.), &c., the quantities will be sufficient for the purposes of most students, but at least twice the amount should be obtained, if supplies have to come from a distance.

Many of the substances are required for use in solution. In Part I, Sect. I, Exercise 5, p. 58 *et seqq.* will be found the general method of dissolving a salt in water; and detailed directions as to the strength of solutions, &c., are given in Appendix B. 26

[An asterisk is prefixed to the names of those substances which the student may prepare himself.]

9	Alcohol, pure, sp. gr. 0.815.
60	„ Methylated, for common purposes.
12	• Aluminium-Ammonium Sulphate ('Ammonia Alum').
6	Ammonium Carbonate, pure.
6	„ Chloride, pure crystallised.
12	„ „ common.
9	„ Hydrate, *solution of, sp. gr. 0.96 (or 0.88) ² , ('Caustic Ammonia').
1	„ Molybdate.

¹ Those who are working in a regular laboratory will probably obtain the necessary chemicals from the common stock. This list is more particularly intended to assist those who are working by themselves, in selecting the substances they will require.

² This is the most concentrated, and best; but care is required in dealing with it. It must be kept in a cool place, with the stopper tied down, and the bottle must be opened cautiously, especially in warm weather.

2	Ammonium Nitrate.
3	" Oxalate.
3	" Phosphate ¹ .
3 ^e	" -Sodium-Hydrogen Phosphate (' Microcosmic salt ').
6	" Sulphide, solution of.
2	Antimony, Metallic.
3	" Trisulphide.
1	Arsenic Trioxide (' White Arsenic ').
3	Asbestos, in long loose fibres.
3	Barium Chloride, pure.
2	" Oxide (' Caustic Baryta ').
1	Bismuth, Metallic.
1	Cadmium Sulphate.
30	Calcium Carbonate, pieces of white marble.
9	" Chloride, thoroughly dried, in lumps.
6	" Fluoride, white fluor spar.
10	* " Hydrate, solution of (' Lime-water ') ² .
6	" Hypochlorite (' Bleaching Powder ').
30	" Oxide, freshly burnt white Quicklime.
20	" Sulphate (' Plaster of Paris ').
3	Carbon Disulphide (' Bisulphide of Carbon ').
2-6	Charcoal, selected pieces.
3	" Animal.
3	* Chlorine, solution of (' Chlorine water ').
1	Chromium-Potassium Sulphate (' Chrome Alum ').
1	Cinnabar (or Vermilion).
1	Cobalt Nitrate.
1	Cochineal.
20	Copper, Metallic; strips of sheet-copper, about 0.5 mm. thick.
3	" filings.
3	" Oxide (' Black Oxide of Copper ').
12	" Sulphate.
	Distilled Water, see p. 70. "
2	Ether.
1	Gall Nuts, in powder.
	Gold, Metallic ; a book of gold-leaf.
3	Grape Sugar.

¹ This salt is preferable, as a test, to sodium-hydrogen phosphate, but is not necessary.

² For the method of making this solution, see p. 65.

- 6 • Hydrogen Acetate, solution of, sp. gr. 1.04 ('Acetic Acid').
 6 • " Chloride, pure concentrated ('Hydrochloric Acid').
 10 * " Chloride, pure diluted.
 30 " Chloride, common concentrated.
 12 " Nitrate, pure concentrated ('Nitric Acid').
 10 * " Nitrate, pure diluted.
 30 " Nitrate, common concentrated.
 6 " Oxalate ('Oxalic Acid').
 12 " Sulphate, pure concentrated ('Sulphuric Acid').
 10 * " Sulphate, pure diluted.
 60 " Sulphate, common concentrated.
 * " Fluosilicate, solution of ('Hydrofluosilicic Acid').
 * " Sulphide, solution of ('Sulphuretted Hydrogen').
 3 Indigo Sulphate, solution of ('Sulphindigotic Acid').
 2 Iodine.
 12 Iron, Metallic; filings, thin wire, and one or two strips of thin sheet-iron; also two or three pieces of the thinnest watch-spring, and a bit of thick clock-spring.
 3 " Perchloride, solution of.
 3 " Peroxide ('Rouge').
 12 " Protosulphate.
 6 " Ammonium Sulphate¹.
 12 " Protosulphide, in lumps.
 1 " Pyrites.
 12 Lead, Metallic; strips of sheet-lead, and some lead wire.
 6 " Acetate.
 3 • " Protoxide ('Litharge').
 3 • " Red Oxide ('Red Lead').
 3 Litmus, solution of ('Archil').
 0.5 Magnesium, Metallic; wire or ribbon.
 3 " Sulphate.
 30 Manganese Dioxide ('Black Oxide of Manganese').
 12 Mercury, Metallic.
 3 • " Oxide.
 3 • " Perchloride ('Corrosive Sublimate').
 1 Nickel Sulphate.
 2 Phosphorus.
 1 " Amorphous ('Red Phosphorus').

¹ This is much to be preferred for making the test-solution, as it keeps for a long time without changing into the persulphate.

3	Platinum Perchloride, solution of.
0.5	Potassium, Metallic.
3	" Bromide.
20 ^f	" Chlorate.
3	" Chromate ('Yellow Chromate of Potassium').
10	" Dichromate ('Red Chromate of Potassium').
3	" Cyanide.
1	" Ferryanide ('Red Prussiate of Potassium').
6	" Ferrycyanide ('Yellow Prussiate of Potassium').
9	" Hydrate ('Caustic Potash').
3	" Iodide.
12	" Nitrate (Purified Saltpetre).
2	" Nitrite.
1	" Thiocyanate ('Sulphocyanate').
1	Silicon Dioxide ('Silica') ¹ .
	Silver, Metallic (a small silver coin will do).
2	* " Nitrate.
1	Sodium, Metallic.
6	" Diborate (Borax).
6	" Carbonate, pure, anhydrous.
10	" Carbonate, pure, crystallised.
20	" Chloride (Common Salt).
23	" -Hydrogen Phosphate.
6	" Thiosulphate ('Hyposulphite').
3	" -Hydrogen Tartrate.
12	" Sulphate.
3	" Sulphite.
3	Starch.
2	Strontium Nitrate.
10	Sugar (Loaf Sugar).
30	Sulphur; Roll Sulphur, and Flowers of Sulphur.
12	Tin, Metallic; in strips and foil ² .
	* " Protochloride (Stannous Chloride), solution of.
2	" Dioxide ('Binoxide of Tin').
3	Tow.
3	Turpentine.
1	Wax (beeswax, or candle).

¹ Pieces of good flint will do.

² Much of what is sold as tin-foil is an alloy of tin and lead. The pure tin-foil may be known by its comparatively rough surface and greater thickness. The sheets of the alloy are much thinner and more pliable, and have a bright polished surface.

- 12 Zinc, Metallic; pieces of sheet-zinc. The purest form of the metal is the Belgian rolled zinc, scraps of which may be procured from any tinman.
- 3 „ Sulphate; the residue obtained in the preparation of hydrogen (Sect. II, Exercise 2) will answer well, if purified by crystallisation.

[Books of printed labels, on gummed paper, including all the substances in the above list and many others, can be obtained from the Publishers of this Book.

For preserving labels on bottles, nothing seems better than the 'celluloid' varnish (celluloid dissolved in amyl acetate), now prepared for photographic and other purposes. This has the advantage of leaving the white paper unaltered in appearance, without the necessity of a previous coat of size or gum. If this varnish is not procurable, the label may be warmed over a lamp-flame or before a fire, and white paraffin wax rubbed over it. This will melt and sink into the paper, making it semi-transparent and thus lessening the legibility of the words, but preserving it from injury by most liquids.]

Advice on the use of the following Exercises.

1. Read over the whole exercise, or at any rate a complete section of it, before beginning work ; in order that you may understand precisely what you are going to do.

2. Look out all the apparatus, &c., required. It need not be *all* actually on the table before you ; in fact, it is generally better that it should not be so ; but everything should be within reach.

3. Have always at hand a text-book on general Chemistry, and refer to it constantly for explanations of chemical reactions, points of theory, &c. The present treatise is intended as a practical companion to such a book, and not in any way to supersede its use.

4. Keep a journal of all that you do ; and in writing it remember that every experiment has an **object**, which should be stated ;—a **mode of performance**, which should be described ;—a **result**, which should be minutely observed and noted down ;—an **inference from the result**, which should be logically drawn.

PART I.

EXPERIMENTS ON THE PREPARATION AND PROPERTIES OF SUBSTANCES.

SECTION I.

PRELIMINARY EXERCISES.

EXERCISE 1.

Fusion and Granulation of Zinc.

Apparatus required.—Iron ladle, with bowl about 7 cm. in diameter; iron spoon; pan or jug filled with clean water; pair of strong pliers; cloth; pieces of metallic zinc.

WHEN melted zinc is dropped into water, the steam formed when it touches the water blows the metal into feathery, tumefied fragments, which from the great surface they expose to the action of a solvent are well adapted for use in such experiments as the preparation of hydrogen gas (Sect. II, Ex. 2). The metal in this form is called 'granulated zinc.'

Put a few small pieces of zinc into the ladle, and place the latter upon a clear fire¹, supporting it on the coals so that the bowl may rest steadily in a horizontal position. Zinc requires a rather high temperature (433°) for its fusion, but when the bottom of the ladle becomes heated to faint redness the fragments of metal will sink down into a fluid mass. When this takes place, add some more pieces of zinc, pressing them down

¹ A Bunsen's burner will answer the same purpose, but not so well. If it is used, the ladle may be supported on an iron tripod, or on the retort-stand, the handle being laid across the largest ring, so that the bowl may be just outside the ring (not resting in it, lest the brass of the ring should melt).

into the fused metal by means of the iron spoon. If any of the pieces of sheet-zinc are too large to go conveniently into the ladle, bend them into a more compact form with the help of the pliers. You will find it much easier to effect this when the metal is made quite hot by being held in front of the fire, or over the lamp; since a sheet of zinc which is stiff and unyielding at the ordinary temperature becomes remarkably pliant when moderately heated. Go on adding pieces of zinc until the ladle is about three-fourths filled, and then leave it to be heated for a minute or two longer, in order that the metal may become quite fluid. The earthy-looking substance, or dross, which floats upon the melted metal, consists of a compound of zinc with oxygen, one of the constituents of the air, and is called zinc oxide. This should, at the last moment, be skimmed off with the iron spoon, so as to leave the surface of the melted metal quite bright, like mercury. You will notice, however, that no sooner has the coating of dross been removed than a thin film of it begins again to be formed, owing to the contact of the air with the strongly heated metal. Now take the ladle off the fire at once, and, holding it about half a metre above the jug of water, pour the liquid zinc in as thin a stream as possible into the water. The liquid metal will, as above explained, be blown into thin films by the steam; and these will solidify as they fall through the water, preserving their fantastic forms.

When all the zinc has been thus granulated, the water in the jug should be poured away, and the zinc should be collected, dried as far as possible with a cloth, then completely dried by being placed on a plate in front of the fire, and kept for use in a wide-mouthed bottle or jar.

EXERCISE 2.

Glass Working¹.

Apparatus required.—Metre rule; pieces of glass tubing, about 6 or 7 mm. in external diameter; pieces of glass rod, rather smaller in diameter; three-square file; fish-tail gas-burner, on iron foot; Bunsen's burner; Herapath's blowpipe.



General Rules to be observed in Glass Working.

Glass must never be either heated or cooled suddenly, unless the special object is to produce a crack. The material is such a bad conductor of heat, that the end of a piece of glass may be raised to a red-heat, while at a distance of 3 cm. from this portion it remains for some time sufficiently cool to be held in the fingers. In consequence of this low conductivity, when heat is applied suddenly to a piece of glass, the parts immediately in contact with the source of heat expand before the heat is communicated to the neighbouring parts, and thus tend to tear the latter asunder. Again, when glass is suddenly cooled, the surface contracts at once, and is torn asunder by the still expanded adjacent portions, which have not had time to lose their heat. It should, therefore, be a rule—


1st, **Never to bring a piece of glass into a flame suddenly**, but to hold it for half a minute, more or less according to the size and thickness of the glass, in the current of hot air above the flame, slowly but constantly turning it round, and heating more of it than is intended ultimately to be brought to a red-heat.

2ndly, **After the work is done, to withdraw the glass very gradually from the flame**, occupying a minute or so in removing it to a distance of 12 or 13 cm. above the flame; then to leave it to cool very slowly in a position protected from currents of air. This is called 'annealing' the glass. It will sometimes be found useful to have at hand a dish of strongly heated sand, into which the hot glass may be plunged and left to cool slowly; and in all cases it is better to err on the safe side, than to risk the breaking of a tube owing to its particles being in a state of tension from deficient annealing.

¹ In this and the succeeding Exercises only the more elementary operations in glass blowing are treated of, such as must be learnt in order to fit up the apparatus required in Sect. II.

3rdly, Always to keep the glass turning slowly while it is in the flame. The heat of a lamp or blowpipe is mainly applied to one side of an object, *viz.* that which is turned towards the wick; while almost all operations in glass blowing require that the piece of glass should be uniformly heated on all sides. If this simple rule be not attended to, it will be found impossible to blow a good bulb and even to make a good bend in a tube. Practice alone, however, can give that steadiness of hand, and *adhesiveness*, as it were, of the fingers to the glass, which will enable the student to rotate a piece of tube which is heated to fusion in the middle, without sensibly distorting the softened part. The portions of the tube on either side of the centre may be regarded as two distinct tubes united by a flexible material; and the object should be, to keep these two tubes in the same straight line, and to rotate them slowly and continuously at the same rate, without laying any stress on the connecting portion. It is generally best to hold the hands under the glass, the upturned forefinger and thumb being chiefly employed in rotating the tube, while the other fingers sustain it at such points that the portions of glass on either side of the heated part are pretty evenly balanced, and have no great tendency to tilt in either direction.

1. To make some elbow tubes (figs. 31, 32), for use in experimenting with gases.

In the first place, a piece of tubing about 6 in. in external diameter,  and 15 cm. in length, must be cut off in the following way:—

Lay a piece of the tubing upon the table before you, holding it down with the thumb and forefinger of the left hand, placed 15 cm. from one extremity. Make a small notch in the tube close to this point with a three-square file, slightly pressing the side of the file against the left thumb, which will thus serve as a guide to prevent the edge of the file slipping along, instead of cutting across, the glass. The notch should be made, not so much by a repeated to-and-fro motion of the file, as by one; or at most two, short forward strokes, combined with as much downward pressure as the tube will bear, the hand being raised a little as the file goes forward, so that it may follow the curve of the surface of the glass. By this means the file will cut deeper into the glass with less injury to itself, than if the edge

were drawn to and fro from point to handle as is usually done; the effect being then rather a rub than a cut. Now take up the tube, holding it with both hands thus, fig. 30 (one hand being on each side of the notch, and the thumb-nails pressing against the glass on the side *opposite* to the notch), and break it

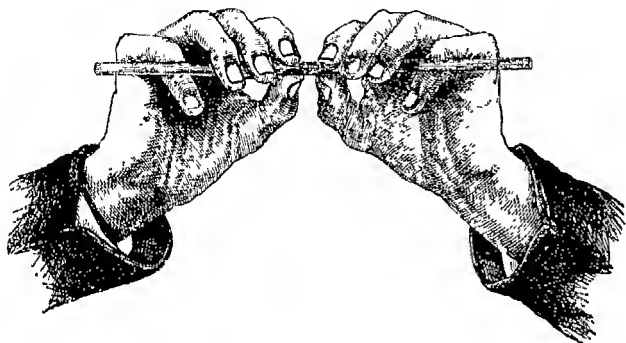


Fig. 30.

asunder precisely as a stick is broken. If the notch has been properly made, the tube will easily break across, the ends being even and at right angles to the length of the tube. If the ends are jagged or sloping, about 1 cm. may be cut off in the way above described; or another piece of tube may be taken.

The edges of the freshly-cut glass, which are extremely sharp, must be rounded off by holding the end of the tube first in the hot air about 4 or 5 cm. above the flame of a Bunsen's burner, and then just within the border of the flame, a little below the top, turning it constantly round and keeping the outer end lowermost, lest vapour should condense in the tube and run down to the hot part, so as to crack the glass. Do not heat the glass so long as to cause the end to sink in, and thus contract the bore of the tube; as soon as the edge is observed to be fairly rounded, the tube should be removed slowly from the flame, annealed in the hot air above it, and allowed to cool, when the other end may be rounded in the same manner.

The tube has next to be bent in the middle to a right angle, as shown in fig. 32 (p. 31).

[For bending the ordinary fusible glass tubing, if its external diameter does not exceed 1 cm., a blowpipe flame is neither required nor so suitable as the flame of a common fish-tail or bat's-wing gas-burner; but if gas is not at hand, a spirit lamp with a large flame may be used.]

Light the fish-tail burner (or spirit lamp); then holding the piece of tube by its extremities, bring it about 7 or 8 cm. above the flame, turning it constantly round and moving it laterally so as to heat about 5 cm. of the middle of it equally on all sides. The flame of a fish-tail burner is flat, and the glass must be held *along*, not across it (fig. 31): the object being to heat a considerable length of the tube, so as to make a gradual bend. After a few

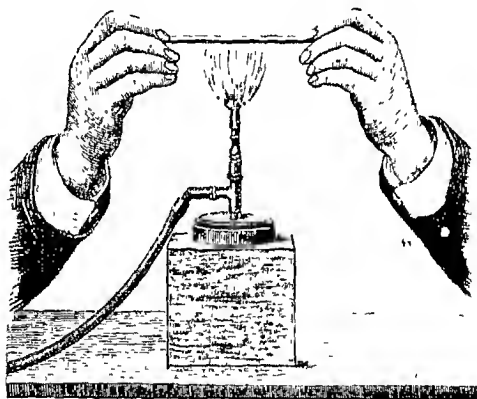


Fig. 31.

seconds, lower it gradually into the flame, still constantly turning it round. If the gas-burner be used, the glass will become covered with soot when immersed in the flame; but this is of no consequence, as the heat of such a burner is never high enough to incorporate the carbon with the glass. When the heated portion becomes soft and yielding, which will take place even before it has acquired a visible red-heat, withdraw it from

the flame, and gently bend it to a right angle, avoiding the use of much force. You will probably find some difficulty at first in making the bend in one plane, *i.e.* so that the bent tube when laid on a flat surface may touch it in every part of its length. The best method of accomplishing this is, to support the tube lightly by its extremities, so that the direction



Fig. 32.

of the bend may be determined mainly by the weight of the tube itself; then, holding it before you so that a line drawn from the eye may pass through both its extremities, gradually approach the hands to each other, as if you were endeavouring to snap the tube in two. Do not attempt to use much force, or to make the bend suddenly, or you will inevitably either flatten the glass on the outer side or wrinkle it up on the inner side; either fault being fatal to the strength of the bend. It will usually be found necessary to heat the tube again in order to complete the bend; and it is better, if there are any signs of wrinkling or flattening, not to attempt to bend it further in that part, but to heat another portion of it a little on one side of the partially-made bend, and to complete the curve in that portion.

Another method of bending small tubes (not more than 6 or 8 mm. in diameter), which practically succeeds very well, is the following:—Heat the tube as above directed until it becomes soft; then hold it steady, just at the top of the flame, withdraw the left hand, and allow the tube to bend by its own weight as far as necessary. It is essential that the tube should be held perfectly still during the bending, and not rotated in any way by the right hand.

The correctness of the angle may be judged of by holding the tube close to, but not actually touching, an ordinary square, or the corner of a table or of the book. When the proper bend is completed, lay the tube on a bit of glass in such a position that the heated portion does not come into contact with any cold surface, and leave it to cool slowly.

While it is cooling you may cut off another portion of the same tubing about 24 cm. long, and after rounding the ends, bend it in a similar way, making the bend, however, not in the

middle of the tube, but about 6 or 7 cm. from one end, as shown in fig. 33. If that end becomes too hot to hold in the fingers it may conveniently be inserted in a hole made in a small cork, which will then answer the purpose of a handle.



Fig. 33.

The tubes thus bent are intended for fitting up a washing bottle or generating flask for gases; and several similar ones with the branches varying in length may be made at leisure moments from any waste bits of tubing, and will be found generally useful, saving much time in fitting up apparatus for any particular experiment.

2. To make a glass jet and a dropping-tube, or pipette.

Cut off a piece of glass tubing (the less fusible the better) about 25 cm. in length and 4 or 5 mm. internal diameter, round off the ends of the tube as directed on p. 29, and heat a portion of it, about 7 cm. from one end, in the flame of a Bunsen's burner¹ (remembering to turn it constantly round), until it becomes quite soft and begins to thicken and contract in diameter: then withdraw it from the flame, and pull the two ends apart by slightly separating the hands, until the drawn-out portion is contracted to an external diameter of 2 mm. (fig. 34). Be careful not to use much force



Fig. 34.

in drawing out the glass, or it will be contracted to a fine thread so thin as to be useless. When it is cool, make a fine scratch with a file at the middle, *a*, of the drawn-out portion, and break

¹ If the glass is very infusible the blowpipe flame must be used, but a Bunsen's burner will generally be found to give heat enough.

the tube at this point. You will then have two tubes, each ending in a jet, the edges of which should be slightly rounded in the lamp flame, and the aperture, if necessary, reduced by holding it for a few seconds longer in the flame, until a large needle would just pass through it. The shorter of these tubes may be kept for use as a jet, in Sect. II, Ex. 2. The longer one will form a very useful 'pipette' for delivering small quantities (such as single drops) of a liquid, in testing. To fill it, dip the jet rather deeply into the liquid (*e.g.* some water in a beaker), and suck the latter up into the tube by applying the mouth to the upper end. When the pipette is nearly full, remove the mouth and immediately press the forefinger (slightly moistened) firmly upon the upper end (see fig. 35); it may then be withdrawn from the liquid, and the pressure of the air will prevent any liquid escaping; but by relaxing the pressure of the finger one or more drops may be allowed to fall, as required.

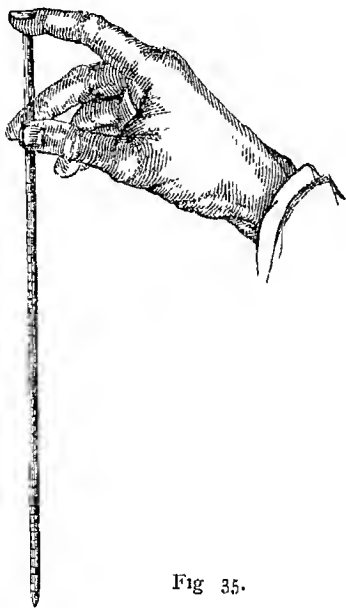


Fig 35.

3. To make a stirring rod.

For this purpose the heat of a gas or spirit lamp is scarcely sufficient; a blowpipe should be used, although a good Bunsen's burner will answer for most kinds of glass, if a blowpipe is not available. The best form of blowpipe is fully described at p. 15, and it will only be necessary here to explain the method of using it so as to produce the greatest effect.

If a Herapath's blowpipe is at hand, the process is simple.

Turn on the gas full, and light it at the mouth of the blowpipe. Then work the bellows gently and uniformly, and gradually reduce the supply of gas, until you have a brush of blue flame about 10 or 12 cm. long.

If you have one of the mouth Herapath's blowpipes, described in the list of apparatus, p. 17, it should be fitted into the tube of the Bunsen's burner and the whole raised on blocks to a convenient height above the table. You should then refer to the Exercise on the use of the Blowpipe, p. 94, and practise the method of keeping up a continuous stream of air, as there described; remembering not to turn on more gas than is necessary to give a moderate-sized brush of blue flame.


[If a spirit or oil lamp must be used, the wick should be trimmed flat and pulled up sufficiently to give a large flame; then with the trimming scissors separate the wick in two parts, and bend each portion sideways so as to leave a clear passage for the air between them. Arrange the lamp and jet so that the latter may lie, pointing slightly upwards, in the line of the passage just formed in the wick, and on a level with the top of it. Light the lamp, and, introducing the jet just within the flame, commence the blast of air. The flame of the lamp will now be almost entirely deflected in the direction of the stream of air; and by pushing the jet a little further into the flame, or drawing it back beyond the margin, any kind of flame may be produced, from a quietly-burning pointed blue cone to a large roaring brush of flame; the former being most suitable for the present purpose. If the flame is ragged or irregular, see whether any filaments of the wick stand in the way of the blast, and if so remove them with the scissors. If this does not cure the defect, the blowpipe jet is dirty or not truly circular, and must be cleaned out by a large needle, or, better, by a small broach.]

Having obtained a satisfactory flame, select a piece of glass rod about 5 mm. in diameter, and cut off a piece about 18 cm. long, as directed in the case of the glass tubing. Hold one end of this piece about 5 cm. in front of the visible flame, turning it constantly round by a twisting motion of the fingers, and gradually bring it just within the apex of the flame, which is its hottest portion. The edges of the glass will soon begin to melt, and the sharp angle will disappear as the glass approaches the liquid

condition. The heat should be continued until the end is perfectly round, and then the rod should be gradually withdrawn from the flame, annealed in the hot air beyond it, and allowed to cool slowly, resting on another fragment of glass, or on the table so that the hot end may project over the edge. As soon as it is cool, the other end may be drawn out so as to form a blunt point (in shape resembling the pipette) by heating it in the flame until it becomes soft, then pressing upon it the end (previously heated) of a short bit of glass tubing or rod, so as to weld them together, and lastly directing the flame on the rod close to the junction, and drawing it out, when soft, precisely as was done in making the pipette. The rod should then be cut at the narrowest part, and the sharp edges slightly rounded by fusion.

EXERCISE 3.

Glass Working (*continued*).

Apparatus required.—Piece of glass tubing, about 5 or 6 mm. external diameter ; pieces of less fusible glass tubing, of the same diameter (the ordinary German glass will, however, do); three-square file; Bunsen's burner; fish-tail burner; Herapath's blowpipe; corks; cork-borers; cork-squeezer, or pliers; narrow-mouthed bottle, about 600 c.c. capacity; rat-tail file; pieces of charcoal, about 3 cm. in diameter, and 6 or 7 cm. long.

1. To fit up a washing bottle, as shown in fig. 36.

In doing this you will have to apply the experience in glass working which you have already gained, and in addition to learn the method of boring holes in corks.

Cut off a piece of glass tubing about 5 mm. in external diameter and 50 cm. in length; hold it horizontally in the hands and heat it (observing the precautions given on p. 27) in the flame of a Bunsen's burner at a point about 15 cm. from the right-hand extremity. As the tube is somewhat long, you will find an advantage in supporting it near the other extremity on a ring of the retort-stand, or other support, fixed

at the same height as the upper part of the flame of the burner. This will render it easier to keep the tube turning between the fingers (p. 28), and to maintain it in the proper position when it becomes soft. Allow the heated portion of the glass to become slightly thickened, then raise the tube out of the flame and draw it out slowly and carefully (waiting until the glass has so far cooled that a little force is required for the purpose), as was done in making the pipette, p. 32. Allow it to cool slowly, and then cut it in two at the middle of the contracted portion. You have now two tubes, the one 35 cm. and the other 15 cm. in length, each terminating in a jet.

Lay aside the shorter tube for the present, and heat the extremities of the longer tube just sufficiently to round off the sharp edges; then (using the fish-tail burner) bend it to an

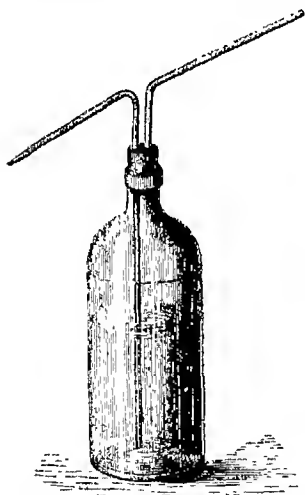


Fig. 36.

acute angle equal to that of the left-hand tube in fig. 36, making the bend about 8 cm. from the jet. While it is cooling take the other tube, cut off the contracted portion at the end, round off the sharp edges of each end in the Bunsen flame, and bend it (using the fish-tail burner) near the middle to an obtuse angle equal to that of the right-hand tube in the figure.

It now only remains to fit these tubes to the bottle by means of a cork perforated with two holes. It will be best, however, to begin by practising the method of making a single hole

in the centre of a cork. Take a good sound cork about 2 cm. in diameter, squeeze it until it becomes soft and elastic (a pair of pliers or nut-crackers may be used instead of a regular cork-squeezer), then take it up thus, fig. 37, between the second finger and the thumb of the left hand, and place the

sharpened end of the smallest cork-borer against it, as near the centre of one end as you can judge. Urge the cork-borer into the cork with a twisting motion, as if you were using a cork-screw. Some care will be required to make the hole straight through the cork, so that it may be truly central. Of the proper direction the eye will be the best judge: and when the cork-borer has penetrated some little way, it will be advisable to turn the cork a quarter round, in order that it may be seen whether the axes of the cork-borer and of the cork are still in the same straight line. If not, a slight pressure on the cork-borer in one direction or the other, while the boring is continued, will set it straight. When the borer has

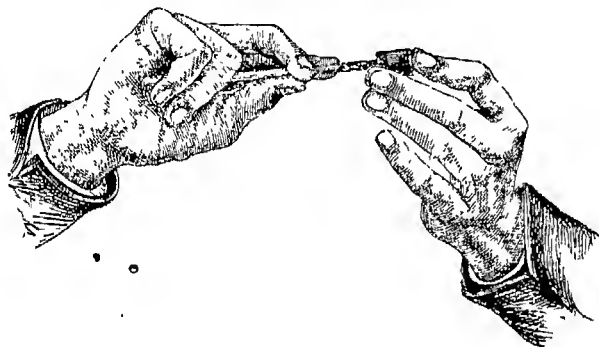


Fig. 37.

penetrated quite through the cork, it may be withdrawn with a twisting motion, and will bring with it a cylindrical plug of cork, leaving a hole, the sides of which should be smoothed with the round or 'rat-tail' file. The plug of cork remaining in the borer may be pushed out by means of a wire which is usually sold with the set of borers for that purpose. It should not be thrown away, as such small corks are often very useful for stopping the ends of drying tubes, and other purposes.

When you have practised in a similar way on one or two other corks, and have learnt to control the direction of the borer, you may complete the fitting up of the washing bottle. Take an ordinary narrow-mouthed bottle holding about 500 or

600 c.c.; choose a cork slightly too large to fit it (since the cork is reduced in size when it is squeezed), and render it soft and elastic by squeezing it. You have now to



Fig. 38.

make two holes in it in the position shown in fig. 38, on opposite sides of the centre, and about midway between the centre and circumference. Take for the purpose a cork-borer rather smaller than the tubing which you have been using, and bore the two holes,

with particular care that each hole does not run into the other or pierce the side of the cork. The cork-borer may be slightly oiled, if thought necessary, but this will be seldom requisite if the end is kept properly sharp. The holes should next be smoothed and slightly enlarged by the rat-tail file, until the end of one of the tubes will just enter them when some little pressure is used. Now pass the longer branch of the longest of the two tubes through the cork, with moderate pressure¹ and a twisting motion, until it projects so far as to reach, when the cork is fitted into its place, nearly to the bottom of the bottle. When this is done, pass one of the branches of the other tube through the other hole in the cork, until it projects 3 or 4 mm. on the other side. Fill the bottle with distilled water, fit the cork carrying the tubes tightly into the neck of it, and your washing bottle is ready for use. Blow gently through the up-turned end of the shorter tube, and see whether a fine stream of water issues from the jet of the other tube. If the jet is found to be too large, it may be easily reduced in size by holding the tip of it (after being freed from moisture) for a second or two in the flame of a Bunsen's burner. Care should be taken not to allow any water to flow down into the jet while it is being heated, which would infallibly crack it.

¹ If much pressure is used the tube is not unlikely to break, and the splinters of glass may cause a serious cut. The hole should never be so much smaller than the tube as to make it necessary to use much force in passing the latter through it. It is a good plan, also, to wrap the tube in a cloth or handkerchief while it is being passed through the hole in the cork.

If no water issues from the jet when you blow air into the bottle, either the aperture is closed up, in which case a small portion of the tip of the jet may be cut off with a file, or there is a leakage of air at the cork. Place a drop or two of water on the cork, and observe whether, on blowing as before, bubbles rise through it. If they do, you may remedy the fault either by pushing the cork more tightly into its place or, if this fails, by taking a new cork altogether, and boring the holes with more care. Never be satisfied with an imperfect apparatus.

[If a larger quantity of water is required at once, as in filling an evaporating dish or small flask, the bottle should be inverted so as to bring the blowing-tube lowermost, from which a stream of water will flow while air enters through the other tube.]

2. To seal a glass tube.

This is the simplest operation in glass blowing strictly so called, *i.e.* in which the assistance of the breath is called in, to mould the glass into shape; and it is one which the student is continually called upon to practise for mending broken test-tubes and making ignition-tubes.

Test-tubes, however, are made of such thin glass that it is by no means so easy as it appears to seal them neatly; and you will find it best to commence work on a piece of readily fusible glass tube about 4 or 5 mm. in internal diameter. Cut off a piece of this tubing about 15 cm. in length, and round the ends in the Bunsen flame. Then, having arranged the blow-pipe so as to give a moderate-sized, steady flame, hold the tube horizontally and bring it gradually into the hottest part of the flame, so that about 1 cm. near the middle may be thoroughly heated. When the glass becomes quite soft, remove it from the flame and draw it out a little by separating the hands,



Fig. 39.

until it assumes the form of fig. 39. Now direct the flame against the part which lies a little to the left of the most

contracted portion, and draw it out further until nothing but a thread of glass remains to connect the two portions of the tube, fig. 40.



Fig. 40.

This thread of glass should next be heated just at the point where it joins the tube on the left hand, when it will fuse and divide, running up into a small knob against the thicker portion of the tube. Lay down the right-hand piece of tube (testing it on another bit of glass, that it may not burn the table), and proceed to make the end of the other piece smooth and round. This is done by directing the flame upon the small projecting knob, which will soon fuse and partially incorporate itself with the surrounding glass. The whole end of the tube will, however, have become contracted and thickened, and must be expanded a little by removing it from the flame and *immediately* forcing air very gently into it from the mouth, until it takes the shape of fig. 41.

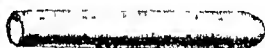


Fig. 41.

Do not blow too hard at first, or heat more of the tube than is necessary, or you will probably expand the sides of the tube into a bulb, which is not your present object: your intention being simply to distribute evenly the thickened glass at the extremity by driving it forwards rather than outwards, and to mould the end of the tube into the regular round form of fig. 41. If this is not accomplished at the first trial, bring the end of the tube again into the blowpipe-flame until it contracts, and blow it out as before, keeping the attention, while blowing, fixed on the heated glass so as to be ready to moderate or stop altogether the supply of air from the mouth, if the glass shows signs of yielding too much.

Now anneal the tube as already directed, and finish the other, or right-hand piece of tube, in a similar way, drawing it out

and rounding it exactly as before. If the bit of capillary tube remaining attached to it is too short or too slight to be used as a handle in drawing out the glass, it should be cut off, and while the end of the tube is heated in the flame, a bit of waste glass tubing held in the right hand should be heated and pressed against it, and the flame directed upon the point of junction. The two pieces will then adhere, and by applying the flame a little more to the left the superfluous glass may be melted and drawn off, attached to the bit of waste glass. Moreover, if the remaining knob be too large to be neatly melted into the bottom of the tube, it may, when soft, be touched with a bit of heated glass and drawn off in a similar way.

After a few small tubes have been thus sealed, larger tubes may be operated on in the same way, a larger blowpipe-flame being employed. Test-tubes broken at the bottom will be found good materials for practising on, and may be mended by drawing off the broken portion and sealing them as above. The glass of which these tubes are made is so thin that it is not easy at first to avoid over-heating them in some one spot, thus producing a mis-shapen end, which is quite inadmissible in vessels which, like test-tubes, are exposed to comparatively sudden changes of temperature. The softened portion should not be drawn out much at first, but allowed to sink in and contract of its own accord, in order to thicken it a little: and especial care must be taken that the bottom is of uniform thickness and well annealed. If there is a crack in the tube, the piece must be broken off by a slight blow; or, better, the crack may be led round the tube as described in the next section, otherwise it will extend itself when the tube is heated.

3. To make 'Ignition tubes.'

These are tubes of difficultly-fusible glass, about 5 or 6 cm. long and 4 mm. in internal diameter, ending in a small bulb, as shown (actual size) in fig. 42 (next page). They are extremely useful for experiments in which the effect of heat upon substances has to be tried, as in the course of Qualitative Analysis.

In the first place a short piece of difficultly-fusible tubing must

be sealed, and the end rounded as above directed; or one of the tubes already sealed may be taken. About 1 cm. of the sealed end of this must be heated strongly and uniformly in the blow-pipe-flame, until it becomes thickened and soft enough to bend by its own weight. It should be prevented from bending or



Fig. 42.

dropping down by turning it continually round in the flame. As soon as it has thus become viscous, take it out of the flame, still turning it round, and *immediately* blow into it until the end has expanded into a bulb about the size of a small marble, as shown in fig. 42. Stop blowing the moment that the bulb has reached the proper size, or the soft glass will almost certainly expand into a large mis-shapen bubble or burst into thin fragments¹. If the bulb is irregular in shape, or 'lop-sided,' the glass has not been *uniformly* heated: most likely because it has not been continually turned round while it was in the flame. If the first attempt is not successful, the bulb may generally be melted down and blown out again; but the glass should not be heated longer or oftener than is absolutely necessary, since many kinds are apt, when kept long at a temperature near melting-point, to become semi-opaque and infusible², and therefore useless.

4. To divide glass by leading a crack along it.

The low conducting power of glass for heat renders it, as has been already noticed (p. 27), very liable to crack from sudden changes of temperature. From the same cause, however, it is easy

¹ If this does happen, you will probably observe brilliant colours in the light reflected from the filmy fragments of glass, like the tints shown by a soap-bubble, and due to the same cause, *viz.* the interference of the rays of light reflected from the upper and lower surfaces, respectively, of the extremely thin plate of glass.

² This change is called 'devitification,' and is probably due to some changes in the composition of the silicates of which glass is composed.

to extend a crack, when once begun, in any desired direction by heating the parts of the glass which lie just in front of the crack; the latter will always extend in the direction of the strain caused by the heat. The method is extremely simple, and will be found especially useful in cutting off the necks of flasks when they are chipped or uneven, and in making evaporating basins or capsules out of broken flasks or retorts.

Suppose, for instance, a Florence flask (or a test-tube) has a neck too uneven to allow of a cork being fitted into it. Arrange the blowpipe¹ to give a moderate-sized flame; take any waste bit of glass rod or tube about 6 mm. in diameter and 7 or 8 cm. in length, and draw it out in the flame as directed in the last section, leaving the end somewhat pointed. Now take the body of the flask in the left hand, the neck pointing upwards, and, having heated the pointed end of the rod to full redness, apply it to the outside edge of the neck, and hold it there for a second or two. It is very probable that a small crack will be thus started, but if not, it may with certainty be produced by removing the heated rod, and immediately touching the spot lightly with a moistened finger or splinter of wood². The crack once begun, press the red-hot end of the rod on the glass a little in front of it, fig. 43, when it will at once extend itself to the heated spot;



Fig. 43.

and by slowly drawing the rod in the direction required, reheating it from time to time in the blowpipe-flame, the crack may be led at first a short distance downwards, and then, turning at right angles, horizontally round the neck so as to cut

¹ A good Bunsen's burner will give heat enough; but it takes a longer time to heat the glass.

² By making a notch with the file in the place and in the direction in which the crack should be, and applying the heated rod to the end of the notch, it is easy to start a crack at once and in the desired direction.

off a ring of glass including the uneven portion. It is generally not possible to carry the crack entirely round the glass until it returns into itself; a small portion of the glass will remain undivided, but after laying down the rod the ring may be readily pulled off, a very slight inequality marking the point where the crack was incomplete.

[A rather better form of termination for the rod, especially when the glass to be cracked is somewhat thick, is that shown in fig. 44. It is made by heating strongly about 5 or 6 mm. of the end of the rod, and then, the rod being held in a slanting direction, pressing it down on any flat metallic surface. The glass will spread out laterally, and by turning the rod half round and pressing it down again in the same way the desired chisel-shaped end will be obtained. In using it the edge should be kept in the line of the crack required,



Fig. 44.

and moved along the surface with slight pressure. The advantages of this form are: 1st, That more of the glass in the desired line is heated at once, so that the crack extends more rapidly, yet under perfect control; 2ndly, That it is easier to lead the crack in an unswerving straight line, the eye being guided by the line of the edge of the tool, than when a blunt point only is used, precisely as a carpenter finds it easier to cut the side of a mortice by a broad chisel than by a narrow one.]

5. To border the necks of flasks or test-tubes.

Having thus rendered the neck of the flask even, it will be desirable not only to fuse the edge in the flame, but to turn it slightly outward so as to form a spreading rim like that of a bottle, which will give it much greater strength when a cork is to be fitted to it. To do this a very simple tool must be first prepared. Select a piece of sound charcoal, free from fissures, about 3 cm. in diameter, and 6 or 7 cm. long. Cut and rasp the end of this to a point like that of a pencil, but more obtuse, the angle at the apex being nearly a right angle. Take the flask in the left hand, and, after heating about 1 cm. of the neck gradually in

front of the blowpipe-flame, cautiously heat the extreme edge in the flame until it softens, turning it constantly round and holding it at right angles to the flame so that the latter may play across the mouth and heat two opposite sides of the glass at once. When the glass begins to soften and sink inwards, take the pointed piece of charcoal in the right hand and press it gently with a twisting motion into the neck. The edge will spread out, and by repeating the operation a border shaped thus, fig. 45, will be obtained, which should be annealed with especial care.

Test-tubes, &c., may be bordered in the same way, but it is best to use a spirit lamp or Bunsen's burner, and not the blowpipe, for heating the edges, on account of the thinness of the glass.



Fig. 45.

EXERCISE 4.

Weighing and Measuring.

Apparatus required.—Balance, and set of weights; Bunsen's holder; test-tube, selected of *stout* glass, about 16 cm. long, and 1.5 cm. in diameter; beakers; washing bottle; pipette; three-square file; writing diamond.

Materials.—Alcohol (methylated spirit); strong hydrogen sulphate (sulphuric acid); piece of glass rod about 7 or 8 mm. in diameter and 3 or 4 cm. in length (the stopper of a bottle will do); bits of lead, iron, cork, and wax, about the same size as the glass; some sand or shot; about 30 cm. of copper wire, No. 18, about 1.2 mm. in diameter; fine cotton or silk; sheet of writing paper; card.

General Rules to be observed in Weighing.

1. Handle the weights very carefully, using a pair of light brass forceps for the smaller ones.
2. Never allow the scales to swing violently about, but keep them steady with the hand while the weights are being put in.
3. Try the weights in a definite order, beginning with the largest, then taking the next smaller, then the next, and so on.
4. Count the weights over twice,—once in the scale-pan, and again as they are being put away in their places,—and put down results at once in your note-book.

1. Examination of the correctness of the balance and weights.

Support the balance in the Bunsen's holder¹, as shown in fig. 46 (next page), at such a height that the pans may be about 3 cm. above the table. Place under the pans a flat ruler (a half-metre rule will do very well), so that by tilting it on its edge they may be steadied when required.

In the first place see that the beam, when free to swing, comes to rest in a horizontal position. This is the case when the pointed index, which projects upwards from the middle of the beam and at right angles to it, lies exactly within the vertical frame from which the beam is hung². If it does not

¹ It will be advisable to put a weight (such as the Argand lamp) on the base of the Bunsen's holder, to prevent the possibility of its falling forward when heavy weights are put in the scales.

² For since the frame by its weight hangs vertical, the index, when parallel to it, must be vertical also. But this index is constructed to be at right angles to the beam; hence when the index is vertical the beam is horizontal.

do so, one of the pans may be dirty, or not hanging fairly from the beam; but if nothing of this kind is noticeable, the construction of the balance may be at fault, and the equilibrium must be adjusted by putting a bit of paper, or tinfoil, in the lighter scale; this must, of course, remain there throughout the exercise.

Next, examine the weights to see if they correspond with, and are correct multiples of one another. If you have the complete set of 100, 50, 20, 10, 10, 5, 2, 2, 1, .5, .2, .2, .1 gm.¹, the following trials may be made.

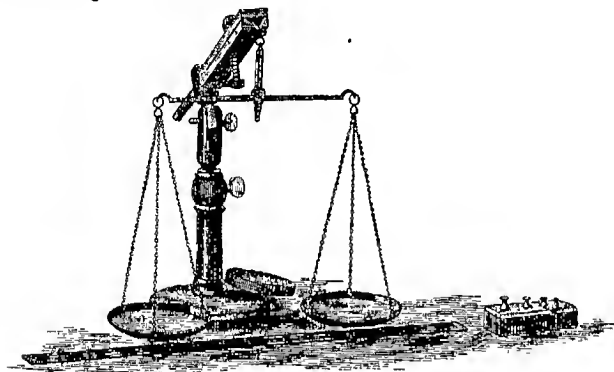


Fig. 46.

1. Place a 10 gm. weight in each scale, and counterpoise it by sand or shot placed in a watch-glass (or pill-box) in the other scale. Then transpose the weights from one scale to the other. They ought still to balance each other: if they do not, the arms of the balance are not of equal length. (If the discrepancy is serious, the balance should be rejected altogether.)

2. Take the counterpoise out of the scale, and substitute for it the other 10 gm. weight. The two weights ought, of course, to balance each other exactly. Absolute accuracy can hardly be expected in common balances and weights, but there should not be an error of more than half a decigram., otherwise the weights should be rejected, or at any rate tested with a standard 10 gm. weight, and corrected.

¹ Suggestions for making weights to fill up any deficiencies in a set are given in Appendix A.

3. Try whether the 2 gm. weight has exactly twice the mass of the 1 gm. weight, in the following way. Weigh out carefully 1 gm. of writing-paper; then put the 1 gm. weight in the same scale as the paper, and see if the 2 gm. weight balances the whole. If it does so, then we are sure that it has twice the mass of the 1 gm. weight, as it should have.

4. Try whether the 2 gm. weight which you have just used balances the other 2 gm. weight.

5. Try whether the $2 + 2 + 1$ gm. weights balance the 5 gm. weight.

6. Try whether the $5 + 2 + 2 + 1$ gm. weights balance the 10 gm. weight.

7. Try whether the two 10 gm. weights balance the 20 gm. weight.

8. Try the 50 gm. weight against the $20 + 10 + 10 + 5 + 2 + 2 + 1$ gm. weights.

9. Try the 100 gm. weight against all those just mentioned.

If you have not a complete set of weights you may still be able to make some of the above trials, and others will suggest themselves. For instance, if you have 1, 2, and 5 gm. weights, 4 grms. of a substance may be weighed out by putting the 5 gm. weight into one scale, and the 1 gm. weight into the other, and then placing in the latter scale enough of the substance to restore equilibrium. This method is called 'weighing by subtraction,' and is constantly useful.

2. Graduation of a test-tube as a measure of cubic centimetres.

The original gramme weight was obtained (see Appendix E) by measuring 1 cubic centimetre of pure water (at 4° C.) and making a piece of metal of such a weight as to balance it. Hence if we put into a tube enough water to balance the 1 gm. weight, this amount of water will measure 1 c.c. (the small correction for temperature may be neglected).

Select a test-tube of stout¹ glass, about 1.5 cm. in external

¹ The glass must be fairly thick, otherwise the file-scratch may sooner or later cause a crack in it. If no thick test-tubes are at hand a suitable tube may be made according to the directions given on p. 39.

diameter and 16 cm. in length. Place a rather large beaker in one scale of the balance, put into it a little sand to steady it and prevent breakage, and support in it the empty test-tube (or hang the tube by a piece of copper wire from the ring to which the chains carrying the scale are attached). Counterpoise them by a beaker partially filled with water (or sand) placed in the other scale. When you have seen that the scales are in equilibrium, put into the scale containing the counterpoise a 1 gm. weight, and pour distilled water into the test-tube from the jet of the washing bottle until equilibrium is restored. If too much water is added, the excess may be removed by a glass rod, or by the pipette which you have already made (p. 32).

Bring the test-tube up to the level of the eye, holding it vertically against the wall, or some other upright support; place the thumb-nail just at the level of the *lowest* part of the curve formed by the surface of the water¹ (see fig. 47),

Fig. 47. and make a slight mark with a file at this level. The mark will then, as already explained, denote a volume of 1 c.c.

Weigh into the tube in a similar manner, 2 grms., 5 grms., 10 grms., and 20 grms. of water, making a file-mark at each point. Finally, empty out the water and make a shallow scratch with the file at each of the marks, guiding the edge of the file by a strip of card held firmly round the tube. The lines may extend round one-fourth of the circumference of the tube, and the figures 1, 2, 5, 10, 20 c.c. may be scratched on the glass close to the proper mark with a sharp point of the file, or, better, with a writing diamond. The tube, fig. 48, is now ready to be used whenever a measure for small quantities is required, and also for determining densities, in the manner next to be explained.

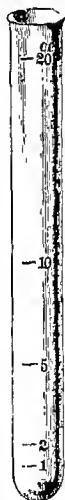


Fig. 48.

¹ This is the best and most sharply-marked level at which to read off a volume of such a liquid as water, and it may be made even clearer by holding behind the tube a white card over the lower half of which has

Determination of Densities.

'Density' means, strictly speaking, 'quantity of matter'; and equal bulks of different substances contain very different quantities of matter. This is generally found out by weighing them. Thus the weight of 1 c.c. of water is, of course, 1 gram.; the weight of 1 c.c. of silver is found to be 10.5 grms. Hence we say that silver has $10\frac{1}{2}$ times the density of water¹.

In practice, water is usually taken as the standard of comparison for liquids and solids, and the 'relative density' or 'specific gravity' of a substance is *the number which expresses how many times a certain bulk of it is heavier or lighter than the same bulk of water.*

Hence in order to determine the density of a substance we have to ascertain,

1. the weight of a definite volume of the substance,
2. the weight of the same volume of water.

Then we have only to find the proportion between the weight of the water and the weight of the substance by the rule-of-three sum;—

$$\text{Wt. of water: } \left\{ \begin{array}{l} \text{wt. of equal vol.} \\ \text{of the substance} \end{array} \right\} : : 1 : \text{density of the substance.}$$

A. DENSITY OF LIQUIDS.

In the case of liquids the process is very simple. A vessel is
 (1) counterpoised so that its own weight may be neglected;
 (2) filled up to a particular level with water, and weighed;
 (3) filled up to the same level with the liquid and again weighed.

The measure you have made is particularly convenient for this purpose, since it is easy to obtain with it a definite volume of any

been pasted a piece of black paper; the boundary line between the white and black being made to coincide nearly with the lowest part of the curve. The latter then appears black and perfectly sharp against the white background.

¹ In illustration of this, a piece of good cork may be cut with a sharp knife into a cube each side of which measures 1 cm., and then weighed: it will be found to weigh nearly one-fourth of a gramme. A cube of lead of the same dimensions (filed and scraped as true as possible) will weigh between 11 and 12 grms.

liquid, and it is clear from the way in which you have graduated it, that the number of cubic centimetres of the liquid taken will express the weight in grammes of the same volume of water, thus saving the trouble of weighing the latter.

Thus if the volume of the liquid is 5 c.c. we know at once without weighing that this volume of water weighs 5 grms.

1. Density of alcohol.

Counterpoise the measuring tube in the balance, in the manner already described; put in 10 c.c. of common alcohol, and weigh it carefully. Put down the weight at once in your note-book.

Then, since it is known that 10 c.c. of water weigh 10 grms. (neglecting the slight correction for temperature) we shall have the proportion,

Weight of 10 c.c. of water : wt. of 10 c.c. of alcohol :: 1 : density of alcohol.

2. Density of hydrogen sulphate (sulphuric acid).

After rinsing out the measuring tube with water and drying it, put into it 10 c.c. of strong hydrogen sulphate and find its density in a similar way, bearing in mind that the substance is very corrosive, and should be handled carefully.

[Other liquids of which the density may be taken are,—strong solution of common salt,—turpentine,—paraffin oil,—mercury (5 c.c. of this will be enough).]

B. DENSITY OF SOLIDS.

In the case of solids there would seem, *prima facie*, to be a great difficulty in getting a volume of the substance exactly equal in size to a given volume of water. It may be done readily, however, by having recourse to Archimedes' principle, that 'a solid when immersed in a liquid loses a weight which = that of the liquid which would occupy its place, i.e. the weight of a volume of the liquid equal to it in size¹.'

All that is required, therefore, is (1) to weigh the solid in air, (2) to immerse it in water and weigh it again in that

¹ Proofs of the truth of this principle are given at the end of this exercise.

position. The difference between the two weights will be the weight of a volume of water equal in size to the solid, and the density can then be found by the usual proportion sum.

EXAMPLES.

1. Density of glass.

Arrange the balance as usual; except that, since the chains

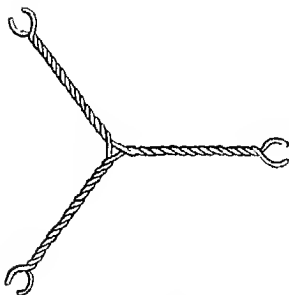


Fig. 49.

or cords by which the scale is hung are likely to get in the way, it will be well to keep them farther out by attaching to them, about 2 or 3 cm. below the ring from which they are hung, a wire frame of the shape shown in fig. 49, made of three pieces of brass or copper wire about 1.2 mm. in diameter (No. 18, wire-gauge) and about 9 cm. long, twisted together; each arm being about 4 cm. long,

Such a frame may be made for each scale, and may remain permanently attached to the balance, as it will be found of great use in preventing the chains getting entangled.

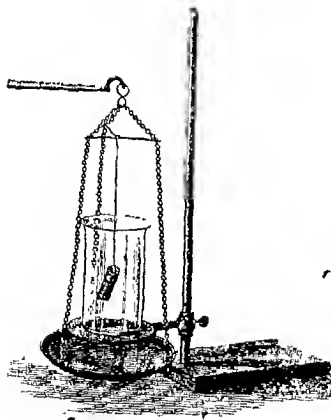


Fig. 50.

Support over one scale a beaker, 5 cm. in diameter, upon a glass plate (or small stoneware gas tray) resting on a ring of the retort-stand, as shown in fig. 50, care being taken to leave just room enough for the scale to rise and fall freely below the retort ring.

Hang a short thick piece of glass rod (or the stopper of a bottle) in a secure noose of the finest cotton or silk, and tie it to the centre of the

three-armed frame above mentioned, so that it may hang freely in the middle of the beaker. Weigh it in this position, and note down the weight at once. Then nearly fill the beaker with water, taking especial care that no drops fall upon the scale, brush away with a piece of wire any air-bubbles which may cling to the solid, and weigh it again. It will now weigh less than before, because of the support which the water gives it, as explained, p. 51. Put down the weights thus:—

weight of glass in air	=	
weight of glass in water	=	
weight of vol. of water equal to glass in size	} =	_____

Then calculate the density by the usual proportion sum;—

Wt. of water : wt. of equal vol. of glass : : 1 : density of glass.

2. Density of lead.

Ascertain this in the same way as described above, taking a leaden bullet, or a strip of thick sheet lead.

Other solids of which the density may be taken, if time permits, are,—a copper or silver coin,—a piece of iron, such as a short thick sciew,—a bit of stone or coal,—a piece of sulphur.

It is advisable to take a good large piece of the substance; otherwise the errors of the balance and weights will be so relatively large as to make the results uncertain.

The calculation may be expressed in the following rule,—

$$\frac{\text{Weight of solid in air}}{\text{Loss of weight in water}} = \text{density of solid.}$$

It is worth observing that you have obtained in the above experiments data sufficient for finding the exact size of the solid, however irregular in shape it may be. You have found the weight of a quantity of water equal in size to the solid. But, since 1 grm. of water measures 1 cub. centimetre, the weight of the water expressed in grammes shows the number of cub. centimetres which it measures, and therefore also the size of the solid in cub. centimetres. Thus if the weight of the water displaced by the glass is 3.2 grms., the size of the glass must be 3.2 c.c.

Additional Experiments.

1. Density of Liquids.

The principle of Archimedes suggests a neat method of taking the densities of liquids, which may sometimes be found useful. It is, simply, to weigh a piece of glass or other suitable solid, (i) in air, (ii) in water, (iii) in the liquid of which the density is required.

Then, as already explained,—

Loss of weight in water = weight of volume of water equal to the solid.

Loss of wt. in the liquid = wt. of vol. of the liquid equal to the same solid.

Thus we have ascertained the weights of equal volumes of water and the liquid, from which the density of the latter is found in the usual way. You may, in illustration, take the density of alcohol by this method, using the solid of which the density has just been found; and of which, therefore, the weight in air and water is already known. Compare the result with that which you previously obtained.

2. Density of solids which are in small pieces, or in powder.

In such cases the ordinary method is clearly impracticable, and we must resort to another method of finding the weight of a volume of water equal to the solid in size. As an example some sand may be taken and its density found in the following way.

Counterpoise the measuring tube on the balance in the usual way, and put into it enough clean dry sand to fill it about one-third full.

Find the weight of the sand, and write down this weight at once on a piece of paper. Thus:—

(i) weight of sand in air =

Then fill up the tube (the sand still remaining in it) with water, to the level of the 20 c.c. mark, see that no air-bubbles cling to the sand, and weigh the whole.

By this last weighing you have found the weight of a mixture of the sand + water, measuring 20 c.c. And if you subtract from this the weight of the sand, the remainder will be the weight of the water you have added to make up the total volume to 20 c.c. Thus:—

weight of sand + water =

– weight of sand alone =

weight of water added =

Now, if the sand was not there, but its place supplied by water,

we should have 20 c.c. of water, which would, of course, weigh 20 grms. And it is easy to see that the difference between 20 grms. and the actual weight of the water you added will be the weight of the water which would be there if the sand was not, *i.e.* the weight of a volume of water equal in size to the sand.

Hence, the next step in calculation will be

$$\begin{array}{rcl}
 & \text{weight of 20 c.c. water} & = \\
 & - \text{weight of water added} & = \text{—————} \\
 \text{(ii)} & \left. \begin{array}{l} \text{weight of water equal in} \\ \text{volume to the sand} \end{array} \right\} & =
 \end{array}$$

Then, since you know already the weight of the sand in air, you have lastly to work out the proportion,—

Weight of water (ii) : weight of equal vol. of sand (i) : 1 : density of sand.

[Other substances suitable for similar experiments are,—small shot,—iron filings,—small bits of sulphur]

3. Density of solids which are lighter than water.

The difficulty in applying Archimedes' principle in such cases is that the unassisted weight of the solid is not sufficient to cause it to remain wholly immersed in the water; the upward pressure of the water being enough to make it float with only so much of its bulk immersed as is equal to the volume of water weighing as much as it does. To illustrate the method of overcoming this difficulty you may take the density of wax in one of the two following ways.

A. Take a piece of wax about as large as a walnut (a bit of wax candle will answer well), and ascertain its weight in air. Then tie it securely to a piece of glass (or lead) of which you have already found the density, sufficiently large to sink it in water. Hang the whole from the wire frame of the balance and weigh it (1) in air, (2) in water, in the usual way. Now, if you subtract the loss of weight which the glass alone showed when immersed in water (already ascertained when its density was taken) from the loss of weight shown by the glass + wax when similarly immersed, the remainder will be the loss of weight due to the wax alone, *i.e.* the weight of a volume of water equal in size to the wax. From this the density of the wax should be calculated in the usual way.

B. A simpler and very instructive mode of finding the density of a solid which is lighter than water, is the following;—

Weigh the solid in air (a piece of wax or a cork about 3 cm. × 2 cm. may be taken). Then place a beaker, about 5 cm. in diameter,

three-fourths filled with water, in one scale of the balance, and counterpoise it by sand in a beaker placed in the other scale. Cut off a piece of brass or copper wire (No. 18 wire-gauge), about 20 cm. long, file one end of it to a point, bend it to a right angle about 7 cm. from the pointed end, and stick the point firmly into the piece of wax



Fig. 51

(or cork) as shown in fig. 51. Lay the wire upon the smallest ring of the retort-stand so that the bent part projects about 7 or 8 cm. beyond the ring, and secure it there by twisting the remainder of the wire about the ring. Bring the stand up to the balance, and carefully lower the solid into the water in the beaker until it is entirely immersed. There will no longer be equilibrium: the solid appearing to push down the scale, though it does not touch the bottom of the beaker. Next put weights into

the other scale until equilibrium is restored, and note down their value. Now, by Newton's Third Law of Motion¹, the upward pressure of the water against the solid is met by an exactly equal downward pressure of the solid against the water in which it is immersed; and since fluids transmit pressure in any direction whatever, the pressure is transmitted to the beaker and the scale is forced down. Therefore the weights you have put into the other scale to restore equilibrium represent the upward pressure of the water against the solid; and this, as already explained (p. 51), represents the weight of a volume of water of the same size as the solid. Thus you have the two *data* required, (1) the weight of the solid itself, (2) the weight of an equal volume of water; and the density of the solid should be calculated in the usual way.

[Other solids of which that density may be similarly taken are—a lump of camphor,—a bit of deal (which must be previously well varnished in order that water may not penetrate it).]

4. Density of solids which are acted upon by water.

Many crystallised salts are of this character, and also such metals as potassium and sodium. It is, of course, impossible to weigh such substances in water; they must, therefore, be weighed in some liquid which does not act upon them, and the density of which is known. Turpentine is in most cases a convenient liquid to use;

¹ "The action of a force is always accompanied by a reaction in the body to which it is applied. This reaction is equal to the force in magnitude and opposite to it in direction."

and as an example the density of alum may be found in the following way.

Take some good clear turpentine and find its density in the usual way. Then hang a lump of alum from the wire frame of the balance, and weigh it (i) in air, (ii) in the turpentine. The loss of weight will, of course, denote the weight of a volume of turpentine equal in size to the alum. Next, the weight of a volume of water equal to this must be found by the proportion sum,—

$$\left\{ \begin{array}{l} \text{Density of the} \\ \text{turpentine} \end{array} \right\} : 1 :: \left\{ \begin{array}{l} \text{wt. of the} \\ \text{turpentine} \end{array} \right\} : \left\{ \begin{array}{l} \text{wt. of an equal} \\ \text{vol. of water.} \end{array} \right\}$$

Thus we have ascertained the weights of equal volumes of water and the alum, and the density of the latter may then be calculated in the usual way.

[Other substances of which the density may be taken in a similar way are—potassium nitrate (saltpetre),—copper sulphate. If the substance is in small crystals or in powder, the method explained in expt. 2, p. 54, must be employed, turpentine being used instead of water.]

The truth of Archimedes' principle referred to on p. 51, may be proved in the following ways :—

A. By theory.

The solid appears to weigh less in water than in air, because the water gives it some support. This support would be equally given to the water which would occupy the place of the solid, if the latter was taken out; *i.e.* to a piece of water of the same size as the solid. But the support given to this water is enough to prevent it from falling through the rest of the liquid (since all parts of a liquid at rest are in equilibrium), *i.e.* is equal to its *whole* weight. Therefore the support given to the solid is equal to the whole weight of a piece of water equal to it in size.

B. By experiment.

Take a small test-tube, fill it about one-third full of water, and make a light scratch with a file at the level of the upper surface of the water in the same way as when the measuring tube was made, p. 49. Take a short thick piece of glass rod, tie a bit of fine cotton or silk round it near one end, and immerse it in the water in the test-tube. The level of the water will, of course, rise; owing to the solid displacing some of it. Mark this higher level by a file-scratch, as before. Then the water contained in the tube between the two marks will obviously be a volume of water equal in size to the solid.

Now take out the glass, dry it and hang it to the wire frame of

the balance inside an empty beaker (just as if its density was to be taken, fig. 5c). Counterpoise it by some sand in a dish placed in the other scale : then fill up the beaker with water until the glass is wholly immersed. The glass will appear to lose some weight ; the question is, how much ? To find out this, fill the test-tube with water up to the higher of the two marks ; then transfer some of this water by a pipette to the scale above which the glass is hung, until equilibrium is restored. Observe how much water has to be taken out of the test-tube to do this ; it is just the volume contained between the two marks on the tube. This amount of water you know to be equal in size to the glass ; and since it has restored equilibrium its weight must be equal to that which the glass appeared to lose. Therefore the weight which the solid appeared to lose when immersed in water = the weight of an amount of water equal to it in size.

EXERCISE 5.

Solution, Evaporation, and Crystallisation.

Apparatus required.—Porcelain mortar and pestle ; scales and weights ; Bunsen's holder ; flask, with flat bottom, about 250 c.c. capacity ; glass measure, holding 200 c.c. ; retort-stand ; sand-bath, with sand ; argand, or spirit lamp ; funnel about 7 cm. in diameter ; filters, 14 cm. in diameter ; beaker ; porcelain evaporating dish, 12 cm. in diameter ; watch-glass ; glass rod, washing bottle, filled with distilled water ; ignition tube (fig. 42, p. 42) ; small gas-bottle ; spatula ; cloth ; writing-paper ; blotting paper.

Materials.—Alum ; sodium sulphate ; quicklime.

Many salts are more soluble in hot water than in cold water¹ ; and when a hot solution, containing as much of the salt as the water can dissolve at that temperature, is allowed to cool, some of the salt separates out, often in the regular geometrical forms called 'crystals.'

1. Crystallisation of alum.

Put into the mortar some lumps of common alum, and reduce them to a coarse powder by first striking them with the pestle

at 0°, at 33°, at 100°,
¹ 100 c.c. of water dissolve 5.22 ; 22 ; 421 grms. of alum.
 " " " " 12.0 ; 322 ; 244 " of sodium sulphate.
 Hence we see that, while sodium sulphate is more soluble in hot than in cold water, its solubility does not increase regularly with the temperature, reaching a maximum at 33°, and then slightly decreasing.

until they are broken up into small pieces and then completing the pulverisation by rubbing these fragments with a circular movement of the pestle (not unlike the motion used in stirring a liquid, but combined with downward pressure), occasionally shaking down to the centre portions of the salt which adhere to the sides of the mortar. When this is done, take two half-sheets of writing-paper, turn up two opposite sides of each, so as to form a trough, and place one in each scale of the balance; they should then be found to counterbalance each other. Into one scale-pan put weights amounting to 30 grms., and into the other bring some of the powdered alum, using a card or spatula for transferring it. Continue to add the salt until the beam turns, then remove any excess of the powder little by little, until the beam remains level, showing that there is the same weight in each scale. Now take out of the scale the paper with the powder in it, and transfer the latter to a flask, as shown in fig. 52.

Place the measure on a level table, and pour distilled water into it until the lowest part of the curved surface of the water

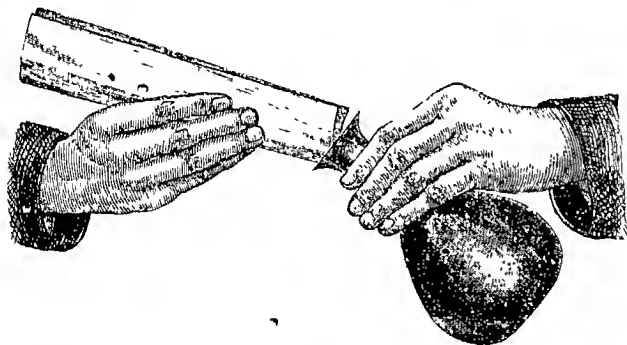


Fig. 52.

is seen to touch the division which marks 150 c.c. The eye should be placed on a level with this division and neither above nor below it, or it will be impossible to obtain a correct measurement. Pour the measured water into the flask and set the latter on the sand-bath, in which should be placed enough sand to form a stratum about half a centimetre in depth. Support the

sand-bath on the largest ring of the retort-stand (taking off the other rings), and place under it the argand burner, the flame of which should nearly, but not quite, touch the bottom of the sand-bath.

While the solution of the alum is going on, you may get ready a filter, or strainer, to separate any particles of dirt which may be present in the liquid. Take a circular piece of filtering paper about 14 cm. in diameter, fold it in half, fig. 53, *a*, and then again at right angles to the first fold, fig. 53, *b*, so that the circle is reduced to a quarter-circle consisting of four thicknesses of paper. Open this out, so as to form a conical cavity, fig. 53, *c*, having three folds of the paper on one side, and one on the other; and place it in a funnel slightly larger than the filter thus folded. The filter should fit the funnel pretty accurately, and may require to be opened out a little more, or, on the other hand, contracted so as to form a more acute cone;

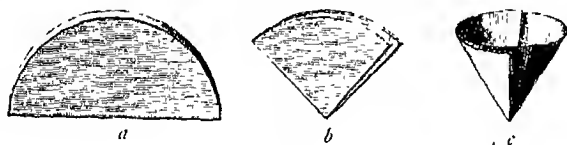


Fig. 53.

but in all cases care should be taken not to injure the point, which, although it requires most strength, is generally the weakest part, since all the creases meet there. It is, in general, best to make the cone of a slightly wider angle than the funnel, so that the filter may fit closely at the upper edge of the funnel rather than at the point. The liquid then runs through more freely and quickly.

Set the funnel in a ring of the retort-stand, and place under it a beaker or other vessel. Moisten the whole of the filter with distilled water, directing a gentle stream, not into the point, but down the thicker part of the side, and allow the water to drain off into the beaker. Meanwhile see if the whole of the alum has by the aid of the heat dissolved in the water, and if not, shake the flask to bring fresh portions of the liquid into contact with the undissolved portion of the salt.

When the salt has entirely dissolved, take away the lamp, take the flask out of the hot sand and put in its place the porcelain dish; turn round the ring holding the funnel, raising or lowering it if necessary, until the tube of the funnel just

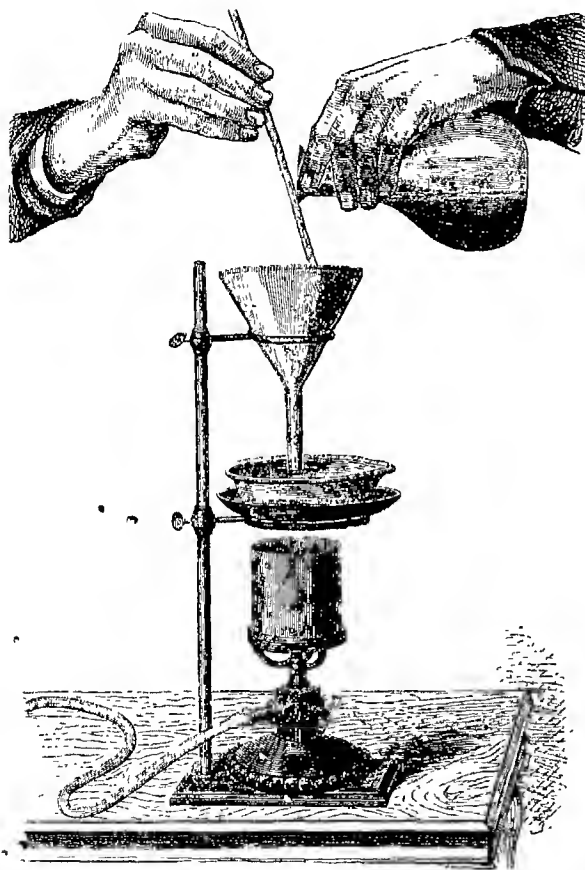


Fig 54.

touches the side of the dish near its rim. Now, grasping the neck of the flask with a cloth, pour its contents along a glass rod, fig. 54, so as to fall on one side of the filter; pouring slowly

eat first, until the filter becomes fully saturated with the solution, but afterwards keeping the filter nearly full. When all the liquid has run through, remove the funnel and filter, and replace the lamp in order to 'evaporate' the solution: *i.e.* to drive off the water until only enough is left to retain the salt in solution at a temperature near the boiling-point. The liquid is then said to be 'saturated' at that temperature. To see when this is the case, dip from time to time a clean glass rod into the solution, place a drop of the liquid on a glass plate or watch-glass and stir it with the rod as it cools. If it deposits minute crystals on cooling, the proper point has been reached. The lamp should then be removed, and the porcelain dish taken carefully from the sand with the fingers (protected by a glove or cloth), and deposited in a cupboard or on a folded cloth laid on the table. Cover it loosely with a piece of paper supported underneath by a short glass rod or tube laid across the dish, passing the rod through a slit in the paper, to prevent its rolling off the dish. The whole should now be left quite undisturbed for six or eight hours at least, in which time a good crop of crystals ought to be formed by the slow cooling of the solution.


When the time above indicated has elapsed, pour off the remaining solution, or 'mother liquor' as it is called, into a beaker, holding a glass rod in contact with the lip of the dish so that the liquid may run down it and not down the outside of the dish. After the last drops have drained away, shake out the crystals on a folded sheet of white blotting-paper, dry them by pressing them gently and repeatedly with fresh pieces of blotting-paper, and examine their shape. You will probably find the greater part of them appear as six-sided lumps thus, , while a few regular



Fig. 55.

four-sided pyramids may be found among them. Both these forms are more or less perfect octohedra, fig. 55, *a*; the four-sided pyramids being easily recognised as the upper halves of octohedra, the lower portions of which

have not been developed, owing to contact with the dish; the hexagonal plates are octohedra lying on their sides, the edges of which have not grown up to a point, as shown in fig. 55, *b*.

[More perfect crystals may be obtained by causing them to form in the middle of the liquid, instead of in contact with the bottom of the dish. For this purpose the crystals already obtained (one or two of the best being reserved for comparison) should be powdered and added to the 'mother liquor' in the beaker, and the latter heated on a sand-bath with occasional stirring until the whole of the salt is redissolved. A piece of lamp-cotton should then be tied by its ends to a bit of glass rod or tube placed across the mouth of the beaker, so as to hang down in the solution to about 2 cm. from the bottom, as shown in fig. 56. The rough surface of this will afford points or 'nuclei' upon which the alum-molecules prefer to deposit themselves, and the crystals can grow equally on all sides. The beaker should be covered with a piece of paper to keep out dust, and left undisturbed for a night. If no good, well-defined crystals are formed on the cotton, the process may be repeated with the substitution of a fresh piece of cotton. The solution should not be left with the crystals for more than a day or so, otherwise changes of temperature may cause the crystals to redissolve and form again in a confused mass at the bottom.]

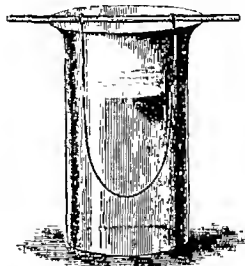


Fig. 56.

2. Crystallisation of Sodium Sulphate.

This should be done precisely as directed above in the case of alum; 60 grms. of sodium sulphate being weighed out and dissolved in 100 c.c. of water. Good groups of crystals are usually obtained in the dish, as shown in fig. 57.

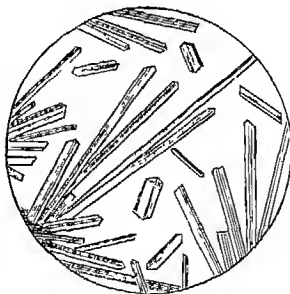


Fig. 57.

Notice how entirely they differ in shape from the crystals of

alum; they appear like thin flattened rods, being, in fact, four-sided prisms belonging to the oblique prismatic (or monoclinic) system, like those of sulphur described in a later exercise.

[Other salts suitable for crystallisation are,—Potassium nitrate (30 grms. in 100 c.c. of water),—Potassium chlorate (20 grms. in 100 c.c. of water),—Hydrogen oxalate (25 grms. in 100 c.c. of water),—Copper sulphate (40 grms. in 100 c.c. of water),—Potassium ferrocyanide (35 grms. in 100 c.c. of water). The different shapes of the crystals should be carefully observed, and each should be referred to its proper crystal-system, an account of which will be found in most text-books.

3. Water of crystallisation.

The crystals of many salts contain a certain proportion of water chemically combined with the substance, which seems essential to its crystalline form. Thus nearly half the weight of crystals of alum and more than half the weight of crystals of sodium sulphate consist of the elements of water. This water is called 'water of crystallisation,' and is retained by different substances with very different degrees of force. Some, such as alum, do not part with it until heated to 100° or even higher; while others, such as sodium sulphate, give off water at ordinary temperatures in moderately dry air. In illustration of these facts,—

(a) Place a small crystal of alum in the bulb of an ignition tube (fig. 42, p. 42), and heat it gently, holding the tube with crucible tongs, in the flame of a Bunsen's burner. The salt will soon melt into a clear liquid, and when heated rather more strongly will give off quantities of water, and finally a white infusible powdery mass will be left, containing no water of crystallisation, which is the true 'anhydrous' aluminium-potassium sulphate.

(b) Place a few crystals of sodium sulphate (dried on blotting paper) in a small wide-mouthed gas bottle, and put in a small lump of quicklime loosely wrapped in blotting-paper, which will by its affinity for water abstract all moisture from the air in the bottle. Put in also one or two crystals of alum for comparison, and leave the whole for some hours. The crystals of alum will

remain unaltered for a long time, while those of sodium sulphate will soon part with their water of crystallisation, becoming (at any rate on their surfaces) a white opaque anhydrous powder. A salt which does this is called an 'efflorescent' salt.

4. Crystallisation of mixtures of salts.

When a solution containing several salts which differ greatly in solubility is concentrated until crystallisation begins, that salt which is least soluble crystallises out first by itself, and can thus be obtained free from the others. In illustration,—

Mix in a clean porcelain dish the solutions of alum and of sodium sulphate which were poured off from the crystals in previous experiments, evaporate the mixture for a short time only, and leave it to crystallise. The crystals which form may easily be recognised as octohedra of alum only, the least soluble of the two salts in cold water¹. This method, of partial crystallisation, is continually employed for the purpose of purifying a crystallisable salt from substances which are more soluble than itself.

EXERCISE 6.

Experiments with Calcium Hydrate.

Apparatus required.—Retort-stand; sand-bath and sand; argand, or spirit lamp; Bunsen's burner; scales and weights; porcelain dish, 8 cm. in diameter; stoppered bottle, holding about 200 c.c. (a small wide-mouthed gas bottle will do); glass rod; two watch-glasses; test-tube, about 1.5 cm. in diameter; test-tube stand; litmus and turmeric papers; writing-paper; cloth; washing bottle, filled with distilled water; lumps of quicklime.

1. Preparation of calcium hydrate.

The salts which you have selected for the last experiment are not only very soluble in water, but also more soluble in hot than in cold water. You may take calcium hydrate as an example of a substance which dissolves only in small proportion in cold water, and is still less soluble in boiling water.

¹ If the evaporation has been carried on pretty far, portions of both salts will separate out, each in its own characteristic crystalline form.

Place a small lump or two of good quicklime (a piece as large as a lump of sugar will be enough) in a porcelain dish, and pour over it four or five drops of distilled water from the washing bottle. The lime, if it is freshly burnt, will in a very short time become very hot and fall to pieces, forming a white impalpable powder. The water disappears entirely, its elements, hydrogen and oxygen, having united with the calcium and oxygen of the quicklime to form a single substance, calcium hydrate¹.

[If it does not become hot in the course of a minute, the reason is that it has absorbed moisture and carbon dioxide by exposure to the air. A lump or two may be put into the hottest part of a common fire, until it has become thoroughly red-hot, then taken out, covered with dry sand and allowed to cool. It must be kept in a well-stoppered bottle.]

2. Solution of calcium hydrate.

Add more water, in successive small portions, to the mass in the basin, until all the lumps of lime have been broken up, and the mass is thoroughly moist: then transfer it with the help of a glass rod or spatula to a stoppered bottle holding about 200 c.c. The last portions may be rinsed in by the aid of a stream of water from the jet of the washing bottle. Fill the bottle nearly to the neck with distilled water, and, after inserting the stopper, shake the liquid for a minute or two, then leave it undisturbed for a quarter of an hour. You will notice that the salt does not dissolve, like the alum, to a clear fluid (although you have added about forty times its weight of water), but that the greater part of it subsides to the bottom of the bottle. Leave the bottle until the next day, occasionally shaking it thoroughly. You will find that even then there is a large quantity of calcium hydrate remaining undissolved; indeed, you will require some positive proof that any of it has been dissolved.

¹ The evolution of heat is due to two causes:—(1) The chemical combination which is taking place. It is a good example of the universal law that heat is evolved during chemical combination. (2) The fact that a liquid (water) is entering into combination, while a solid (calcium hydrate) is the sole product. For in all cases in which a liquid becomes a solid, heat is evolved.

3. Properties of calcium hydrate.

Take out the stopper, wipe the inside of the neck of the bottle with a clean cloth, and half fill a moderate-sized test-tube with the solution, inclining the bottle very gently so as to avoid disturbing the sediment. Hold the test-tube up to the light, in order to see if there are any solid particles floating in the liquid. If such is the case, the liquid may be filtered into another test-tube. The following experiments should be tried with the clear solution:—

1. Try whether anything has really dissolved in the water.

Pour a few drops into a watch-glass; place the latter upon the sand-bath, supported as before on a ring of the retort-stand, and evaporate the liquid to dryness, proceeding meanwhile with other experiments. For the sake of comparison you may evaporate in another watch-glass (placed on the same sand-bath) a little of the distilled water which you have been using. When all the water has been driven off, you will find that in the former case a solid white residue is left on the watch-glass, in the latter case there is no residue whatever, or at all events a mere trace. The occurrence of such a residue is a conclusive proof that something has been dissolved by the water.

2. Taste a drop or two of the liquid. You will find that it is not tasteless, like pure water, but has acquired a sharp caustic taste.

3. Try its action on test-paper.

Lay strips of blue litmus, reddened litmus, and turmeric paper on a white plate, and place on each, with a glass rod, a drop of the solution. It will not alter the blue litmus, but will turn the reddened litmus blue and the turmeric a brownish red. A substance which does this is said to have an 'alkaline reaction.'

4. Try the effect of heating the solution.

Heat gently over a Bunsen's burner, fig. 58 (next page), the test-tube containing the remainder of the solution of calcium hydrate.

[The operation of heating a test-tube in the naked flame requires some care, otherwise the tube may crack, or its contents may be thrown out, owing to the sudden formation of large bubbles of

vapour at the bottom of the tube. Hold the tube in a slanting position, turning it round between the fingers and moving it to and fro in the flame, so as to distribute the heat over as large a surface as possible. If the tube becomes too hot to be held between the fingers, a simple and convenient holder is obtained by folding half a sheet of writing-paper into a band about 2 cm. in breadth. This should be passed round the tube near its mouth, and held (close to the tube) between the forefinger and thumb, as shown in fig. 58¹. Remember, moreover, that the test-tube should not, as a rule, be more than *one-third* full, and that no heat must be applied to the part of the tube above the level of the liquid; otherwise, if the colder liquid should reach this part, the tube will be almost certain to crack. When the liquid has nearly reached the boiling-point, remove the tube from the direct flame and hold it at the side or above the flame, occasionally shaking it to promote the formation of bubbles of vapour.]



Fig. 58.

Observe that the liquid, as the temperature rises, becomes milky, a solid substance, or 'precipitate,' being formed in it. This is owing to the fact that calcium hydrate is much less soluble in hot than in cold water². A solution, therefore, of

¹ The jaws of a Bunsen's holder, fig 3, taken out of the socket, also form an excellent holder.

² 100 c.c. of water dissolve at 15°, 0.173 grms.; at 100°, 0.083 grms. of calcium hydrate.

calcium hydrate, which is saturated at the ordinary temperature, will deposit a portion of the substance, when it is heated.

Cork the tube and cool it by immersing the lower portion of it in cold water, shaking it occasionally. The greater part of the turbidity will, after some little time, disappear: the calcium hydrate being again dissolved.

From the above experiments you have learnt that calcium hydrate possesses the following properties:—

1. It is slightly, but only slightly, soluble in water.
2. It is not volatile, but is left as a solid residue when its solution is evaporated.
3. It has a sharp, burning taste.
4. It has an alkaline reaction on test-paper.
5. It is less soluble in hot than in cold water.

Use of calcium hydrate as a test.

[A test means an experiment, or a material for an experiment, by which we examine an unknown substance to find out what it is.]

This solution of calcium hydrate (or 'lime water,' as it is often called) is chiefly used to detect the presence of carbon dioxide ('carbonic acid'), since when it is brought in contact with this gas it becomes cloudy, owing to a white insoluble substance, calcium carbonate or chalk, being formed. Hence it is called a 'test' for carbon dioxide.

You may illustrate this use of it, and at the same time prove that carbon dioxide is present in the breath, by putting a little of the solution into a small beaker, and blowing into it for a few seconds through the long branch of an elbow tube, when the clear liquid will gradually become milky.

[Pour off the rest of the solution of calcium hydrate into a clean bottle holding about 100 c c., inclining the bottle which contains the solution very gently, in order to avoid disturbing the solid substance at the bottom. This operation is called 'Decantation,' and will be again alluded to in Exercise 9. Be careful to cease pouring before any turbid solution finds its way into the second bottle (if any floating particles are noticed, the whole must be filtered); close the latter with a good cork or stopper, and, after placing a label on it, put it away for use in future experiments.]

EXERCISE 7.**Distillation.**

Apparatus required.—Stoppered (or plam) retoit, about 200 c.c. in capacity; retort-stand; sand-bath with sand; argand, or spitt lamp; small flask; porcelain mortar; Bunsen's holder; funnel, 10 cm. in diameter; beaker; test-tube stand; test-tubes in basket; watch-glass; washing bottle with distilled water; wooden blocks; blotting-paper; lamp-cotton, or tow.

Solutions of barium chloride, silver nitrate, ammonium oxalate, hydrogen nitrate (dilute), ammonium hydrate, calcium hydrate.

Distillation is the process of converting a volatile liquid into vapour, condensing the vapour again into a liquid, and collecting the product or 'distillate.'

It is very frequently used in chemical work for separating a more volatile from a less volatile substance. For example, alcohol may be thus separated from water, and water itself may be, as will be seen in the following exercise, separated from various impurities which unfit it for use in the laboratory.

An apparatus for distillation consists of three parts :—

1. A boiler; for which, in laboratory work, a glass retort is generally used.
2. A condenser; for which the long neck of the retort, kept cool by being wrapped in paper soaked in cold water, will serve sufficiently well¹.
3. A receiver; such as a glass flask.

Distillation of Water.

Select a stoppered retort with a long neck; place it upon the sand-bath (containing a little sand), supported upon the largest ring of the retort-stand at such a height as to allow the lamp to be placed under it. Put over the tubulure the smallest retort-ring, to hold the retort steady in its place. This will be most conveniently done if the rod of the retort-stand is placed behind the retort, as shown in fig. 59. Pass the beak of the retort

¹ A preferable form of condenser, known as 'Liebig's condenser,' is described in Appendix A.

into a clean flask, placed in a slanting position in the porcelain mortar, and support the latter on wooden blocks at such a height that there may be a gradual fall from the point at which the neck joins the body of the retort to its outer extremity.

Now fill the retort about half full (not more) of common water, using a funnel passed through the tubulure and taking care that no water passes down the neck of the retort.

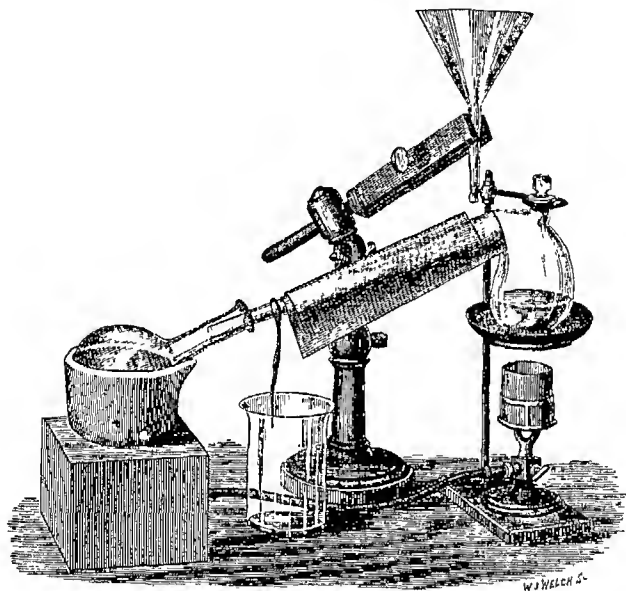


Fig. 59.

[If you have to use a plain retort, the water must be put in before it is arranged in its place. For this purpose, lay a folded cloth upon the table and place the retort upon it, supporting its neck in a vertical position by a Bunsen's holder; then pass a thistle funnel down the neck and pour through this the proper quantity of water.]

Now light the lamp and put it under the sand-bath. While the water is being gradually heated, the arrangement for condensing the steam should be set up in the following way.

Take a piece of blotting-paper about 14 or 15 cm. broad and

about three-fourths as long as the neck of the retort; fold two of its adjacent corners inwards so as to give the paper the following outline (fig. 60); wet it thoroughly, and place it over



Fig. 60.

the neck of the retort with the folded corners underneath, so that while the narrower part of the paper lies upon the broader part of the neck, the lower part of the neck may be completely enveloped by the paper, the two unfolded corners (pressed close together) hanging down some way below it. Next, take a strip of blotting-paper about 10 cm. in breadth and somewhat shorter than the first strip, fold it, in the direction of its length, into the shape of the letter Λ , and place it like a saddle upon the first wrapper. Just beyond the lowest end of the folds of paper, twist round the neck of the retort a few strands of lamp-cotton or of tow, thoroughly wetted, the end of which should hang down 10 or 12 cm. The object of this is to prevent any water which may trickle down beyond the paper from passing any farther down the neck of the retort and entering the receiver¹. Underneath the end of this piece of cotton is to be placed a beaker or jug to catch the waste water. Directly over the upper extremity of the paper-wrapping support in the Bunsen's holder a large funnel, the neck of which has been partially plugged up by a bit of paper or tow, so that water will only issue from it in drops. This should be tried before the funnel is arranged in its place, by holding it over a basin or sink, pouring in some water, and pushing in or pulling out the plug of tow until the drops follow each other not too quickly to be counted.

After fixing the funnel in the Bunsen's holder (which should have a weight put on the wooden base behind to prevent any chance of its toppling over) fill it with common water, and see that the drops fall slowly and regularly from its beak upon the upper end of the blotting-paper, and that the water, after saturating the paper, finds its way into the beaker, and not into the receiver. You will now see the use of the upper strip of

¹ A ring of cork, fitted on the neck of the retort, will do as well, or better.

paper; it serves as a channel to guide the drops of water and to distribute them regularly over the paper-wrapping underneath.

The water in the retort will soon begin to boil, and the steam, passing over into the colder parts of the neck, will be re-converted into water which will collect in drops and run down into the receiver. When twenty or thirty drops have thus distilled over, withdraw the receiver (holding the neck of the retort steady with one hand), and pour away the liquid which it contains; since the first portions which come over are liable to contain impurities derived from the neck of the retort. When the last drop has drained away, replace the receiver in its former position and continue the distillation until about three-fourths of the water in the retort has passed over, proceeding meanwhile with the experiments given below. Pour, from time to time, some cold water into the large funnel so as to keep it nearly full. Be particularly careful to regulate the heat so that the water may not boil so violently as to splash over into the neck of the retort, and thus be carried down into the receiver. If, in spite of care, it boils unsteadily, with 'bumping,' owing to the sudden formation of large bubbles of steam in contact with the more strongly heated portions of the retort, it will be advisable to remove the lamp, to wait until the temperature of the water has sunk a few degrees, and then to introduce into the body of the retort a fragment or two of charcoal, or a bit of crumpled platinum foil. This will, in consequence of its numerous points and edges, materially assist the formation of smaller bubbles of steam, and when the lamp is replaced the boiling will go on more quietly.

Experiments with Common Water.

Ordinary spring water or river water almost always contains such substances as sodium chloride (common salt), calcium sulphate (plaster of Paris), calcium-hydrogen carbonate, &c., which it has dissolved from the rocks through which it has passed. You may, while the distillation is going on, try whether any of these are present in the water which you are using in the following way:—

- Place four clean test-tubes in the stand, and fill each about one-third full of the same kind of water as that which you have taken for distillation.

[In pouring a solution from a bottle into a test-tube, it should be a rule never to allow drops of the liquid to run down the side of the bottle. Apart from the unsightly appearance of a bottle encrusted with crystallised salts, the labels are likely to be obliterated or washed off, and shelves and tables will be damaged. These inconveniences may be entirely avoided by the simple method of pouring which is illustrated in fig. 61. The test-tube, into which the liquid is to be poured, is held near the top between the third finger and little finger of the left hand. The stopper, grasped by the forefinger

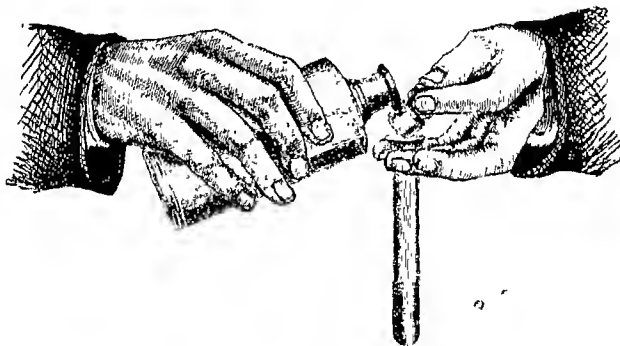


Fig 61.

and thumb of the same hand, is loosened and wetted with the solution by slightly inclining the bottle; it is then taken out, drawn across the neck, so as to leave a wet track for the liquid to follow, and held against the neck of the bottle, while the test-tube is brought directly under it. The stopper then (like the glass rod in fig. 54, p. 61) forms a prolongation or lip down which the liquid runs, not a particle finding its way down the side of the bottle. Besides the greater facility with which drops may be measured out, this method has the further advantage, that the stopper is never out of the hands, and hence there is no danger of the solution being contaminated by impurities taken up by the stopper from a dirty table.]

(a) Test for the presence of a Sulphate.

Add to the contents of one test-tube five or six drops of

dilute **hydrogen nitrate** (nitric acid), and then one drop of solution of **barium chloride**; shake the test-tube, and hold it up to the light. If a *white cloudiness* or deposit (called a 'precipitate') is produced at once, or in the course of a few minutes, it is a proof that the water contains a **SULPHATE**.

(b) **Test for the presence of a Chloride.**

Add to the contents of another test-tube five or six drops of dilute **hydrogen nitrate**, and then one drop of solution of **silver nitrate**. If a *white cloudiness* or 'precipitate' is produced, the water contains a **CHLORIDE**.

(c) **Test for the presence of a compound of Calcium.**

Add to the contents of the third test-tube three or four drops of solution of **ammonium hydrate** (ammonia), and then one drop of solution of **ammonium oxalate**. If a *white cloudiness* or precipitate is produced, the water contains a compound of **CALCIUM**¹.

(d) **Test for the presence of Carbon Dioxide or a Carbonate.**

Add to the contents of the remaining test-tube about 1 c.c. (a small tea-spoonful) of solution of **calcium hydrate** (lime-water). If a *white cloudiness* or precipitate is produced, it is, as you have already seen, p. 69, a proof that the water contains **CARBON DIOXIDE** or a **CARBONATE**.

[For experiments on the 'hardness' of water, see under **CALCIUM**.

For a test for the presence of organic matter in water, see under **MANGANESE**.]

Tests of the purity of Distilled Water.

By this time sufficient distilled water will have collected in the receiver to be examined by the same tests, in order to see whether the process of distillation has freed it from impurities (if any have been found).

Place four clean test-tubes in the stand, pour into each some

¹ If the water which you have used is fresh spring-water, and if, from experiment (c), you have discovered that a calcium salt is present, you will probably find that, as the distillation proceeds, the water in the retort becomes turbid, and a white deposit is formed. The reason of this will be explained in the Exercise on Carbon Dioxide (p. 191).

of the distilled water, and repeat experiments (a), (b), (c), (d). The water should give no cloudiness or precipitate in any of the above experiments, and if a few drops are poured into a clean watch-glass and evaporated to dryness on the sand-bath no solid residue should be left; otherwise it is most likely that the water in the retort has boiled too rapidly, and a portion of it has splashed over, or has been carried over as spray into the receiver.

Before the water in the retort has wholly evaporated, you should stop the distillation by removing the lamp, and withdraw the receiver, resting the beak of the retort temporarily upon the edge of the mortar. The retort and the rest of the apparatus should now be cleaned and put away for future use. If there is any deposit in the retort which cannot be removed by water alone, a few drops of dilute hydrogen chloride (hydrochloric acid) will at once dissolve it¹.

EXERCISE 8.

Chemical Action.

Apparatus required.—Bunsen's burner; test-tubes in basket; test-tube stand; cedar spills; glass rod; platinum foil; porcelain dish 5 cm. in diameter; stoneware gas tray (No. 26, p. 10); crucible tongs; glass mortar; porcelain mortar; china plate.

Mercury peroxide; solution of copper sulphate (blue vitriol); granulated zinc; dilute hydrogen chloride; phosphorus; iodine; copper filings; clean strip of sheet iron, 15 cm. \times 1 cm.; flowers of sulphur; mercury perchloride ('corrosive sublimate'); potassium iodide; solutions of ammonium chloride ('sal ammoniac'), silver nitrate ('lunar caustic'), mercury perchloride, ammonium carbonate, calcium chloride.

[For the solutions above-mentioned the ordinary laboratory test-solutions will answer, prepared as directed in Appendix B.]

ANALYSIS.

The first and chief work of the chemist is, to examine the

¹ It will be scarcely worth your while to attempt to distil for yourself all the water you will require. You will in all probability be able to obtain it at the nearest chemist's shop at a cost of 2d. or 3d. per quart. But the water which you buy should in all cases be examined by the above tests, and rejected at once if any impurity is found in it.

composition of all kinds of matter. When anything is brought under his notice, he tries by various forces to break it up into two or more substances unlike itself and each other, and to break up these again into others, until at last he has *dissected* things, as it were, into a number of substances which he is unable (with his present means) to separate further. These simple substances are called 'Elements,' and the process of separating bodies into their elements is called 'Analysis.'

In the work of analysis several forces are used, and the following experiments will illustrate their employment.

I. ACTION OF HEAT.

Place about 0.5 grm. (as much as will lie on the end of a penknife) of the red substance called 'red oxide of mercury' in a moderate-sized dry test-tube, and heat it strongly over a Bunsen's burner, supporting it slanting in a Bunsen's holder, as shown in fig. 62. The mouth of the tube should be closed *loosely* by a cork or a cover of paper; and the tube should not be held so tightly in the holder as to prevent its being turned slowly and continuously round while being heated, in order to avoid melting it. The substance will become darker in colour, and, as the heat approaches redness, a bright metallic ring will be formed in the cool part of the tube. Continue the heat until the whole of the red substance has disappeared, then light a cedar spill, blow it out, and while its end is still glowing plunge it into the tube. It will burst into flame. This property

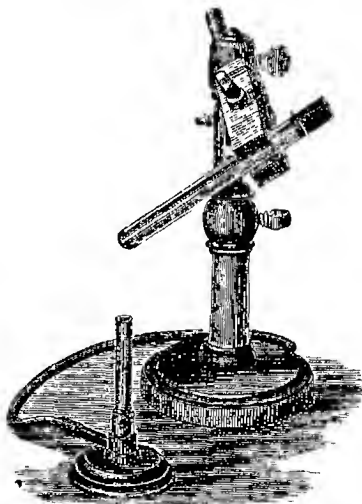


Fig. 62.

of rekindling a glowing splinter of wood is characteristic of oxygen, and on trying other experiments we should find that the properties of the gas in the tube agree altogether with those of the substance which has been called oxygen. Next, examine the mirror-like deposit in the tube; you will see that it is a cluster of small liquid globules which, on being touched with a glass rod, run together into a larger globule possessing a bright metallic lustre and considerable weight. These properties, together with others which you would discover on further examination of the deposit, coincide with the properties of the substance called mercury. Moreover, if we weigh (*a*) the red substance before heating it in the tube, (*b*) the gas evolved, and (*c*) the metal deposited, we should find that the weight of the original substance was equal to the sum of the weights of the gas and of the metal obtained from it.

Further, on making other experiments with the gas and the metal, we should find it impossible, with our present means, to break them up into simpler forms of matter.

Our inference, then, is that the red substance is composed of the element oxygen and the element mercury. In what state these substances exist in the compound we cannot say; all that we know is, that they, and they only, can be obtained from it.

Especial notice should be taken of the difference between the *physical* action of such a force as heat, and the *chemical* action of the same force.

When heat was communicated to the red mercury oxide, the substance changed its size, becoming larger than before: and on further heating it became altered in its power of reflecting rays of light: in other words, it changed its colour. But these were only temporary changes: when the heat was withdrawn the substance recovered its former size and its former colour. Such an action is a physical one only.

But when the communication of heat was carried further, a change of a totally different character took place; the original red powder disappeared, and two totally different substances appeared,—a colourless gas, and the vapour of a brilliant metal.

Further, on withdrawing the heat, the original red substance was not again obtained.

We have here, in fact, a *permanent* change, and this is characteristic of a chemical action.

[Keep the tube with the deposit of mercury for another experiment, p. 82.]

II. ACTION OF ELECTRICITY.

Lay a piece of platinum foil (the strip used for blowpipe experiments, No. 18, p. 8) in a porcelain dish, and pour upon it about 20 c.c. of solution of copper sulphate (blue vitriol). The surface of the platinum foil will be quite unaltered; but if a bit of zinc is dropped into the solution and pressed closely into contact with the platinum, a coating of a red metal, which can be no other than copper, will be in the course of a few seconds deposited upon the platinum; as will be seen if the piece of foil is taken out of the liquid¹.

The reason is, that an electric current has been set up by the contact of the zinc and the platinum; and this, in passing through the solution, has separated the copper from its combination with sulphur and oxygen. The metal is thrown down on the platinum: the sulphur and oxygen are liberated at the surface of the zinc, with which they combine.

[After taking out the platinum foil², leave the zinc in the solution of copper sulphate until the next experiment has been performed.]

III. ACTION OF CHEMICAL AFFINITY.

This is, perhaps, more generally used than any other: the principle being to overcome the attraction between two elements, *A* and *B*, which form a compound, by acting upon the compound with some substance, *C*, between which and *A* there is a stronger affinity than there is between *A* and *B*.

¹ The deposit will scarcely be seen before this is done; since the blue liquid absorbs nearly all the red rays, which are the only ones the copper can reflect.

² The platinum may be cleaned from the film of copper by pouring on it a few drops of strong hydrogen nitrate, which will dissolve the copper. It should then be washed thoroughly with water.

Then the compound is broken up, or 'analysed,' *A* combining with *C*, while *B* (if it has itself no tendency to combine with *C*) is left free and uncombined.

(a) Put about 10 c.c. of dilute hydrogen chloride (hydrochloric acid) into a test-tube supported vertically in a Bunsen's holder, drop in a piece of zinc, and cover the mouth of the tube with a bit of paper or card. An effervescence will begin at the surface of the zinc, and a gas will be given off which will catch fire when a lighted match is introduced into the tube, and may be proved to have all the other properties of hydrogen.

The reason is this:—hydrogen chloride is composed of two elements, hydrogen and chlorine; chlorine has a greater affinity for zinc than it has for hydrogen; therefore it leaves the hydrogen and combines with the zinc, while the hydrogen (having itself no affinity for zinc) is liberated as gas.

If you leave the liquid until all action is over, and then, after filtering it from any undissolved particles, put it into a porcelain dish and evaporate it to dryness, you will obtain a white residue which is the compound of zinc with chlorine (zinc chloride).

(b) Examine the zinc which was left in the solution of copper sulphate used in the previous experiment on the action of electricity. It will be found to be covered with a dark powdery deposit of metallic copper. The zinc has, in fact, decomposed the copper sulphate, combining with the sulphur and oxygen to form zinc sulphate, and displacing the copper, which is deposited in the metallic state.

The above are examples of a very common form of chemical action called 'Substitution,' or 'Replacement.'

B. SYNTHESIS.

Having obtained these simple substances or elements, the chemist proceeds to examine the way in which they combine with each other to form compounds, and the action which these compounds have on one another to produce other compounds.

This process of forming compounds is called 'Synthesis,' and depends upon the chemical affinity or attraction between particular substances which has been illustrated in the two last experiments. This affinity is by no means universal: we may intimately mix some substances together and yet they will remain simply mixed, without giving any proofs of a tendency to combine.

The following characteristics enable us to distinguish between a mere mixture and a true chemical compound.

If, on putting two things together, we find,

1. that heat is given off,
2. that there is a sudden change in appearance, more or less complete,
3. that the two substances originally taken disappear permanently, and can no longer be distinguished as lying side by side in the mixture, while the resulting product is to all appearance a *single* substance, alike in every part,

then we may be sure that chemical action has taken place, and that a true chemical compound has been formed by the union of the elements.

Examples.

A. ACTION OF ELEMENTS ON ONE ANOTHER.

1. Combination of Phosphorus with Iodine.

[In all experiments where phosphorus is made use of, great care must be taken to prevent its catching fire. It must never be allowed to remain for more than a few seconds out of water, and should always, if possible, be held with the crucible tongs, not with the fingers. A jug of water should always be within reach to extinguish it in case it should accidentally inflame, as may happen in a hot room. All residues from experiments in which phosphorus has been used should be kept under water until they can be thrown away, out of doors.]

Take a piece of phosphorus out of the bottle with a pair of crucible tongs, and place it in a gas tray (or small dish) filled with water. Cut off a *small* piece, not larger than half a pea, dry it carefully by pressing it gently between folds of blotting-

paper, and put it on a plate. Then place in contact with it one or two crystals of iodine. The two substances have so strong an affinity for each other that they will almost immediately combine; so much heat will be given off as to cause inflammation of the mass, and a scarlet compound (called 'phosphorus iodide') will be formed, totally unlike either of the elements, and in which it would be impossible to distinguish the separate particles of iodine and phosphorus, even by a powerful microscope.

[As soon as the experiment is concluded, cover the residue in the plate with water until it can be thrown away, preferably on ashes or earth out of doors.]

2. Combination of Mercury with Iodine.

The affinity between these substances is hardly strong enough to enable them to combine when merely placed in contact. But heat (the same force, be it observed, that you have already used to decompose compounds) will readily cause combination to take place between them.

Take the tube containing the deposit of mercury which was obtained in a former experiment, p. 79, put into it one or two crystals of iodine, and heat gently first the deposit of mercury on the sides, and then the iodine at the bottom of the tube. The iodine will volatilise as a splendid purple vapour and will combine with the mercury (with a crackling sound due to the sudden evolution of heat), forming a bright scarlet substance called 'mercury iodide,' which is often used as a paint.

3. Combination of Copper with Sulphur.

In this case a much stronger heat is necessary to cause combination.

Weigh out, on paper, 1 grm. of copper filings and 0.5 grm. of sulphur; mix them together in a mortar and put the mixture into a moderate-sized test-tube. No combination takes place at once, as in the first experiment, and it is easy to distinguish the red particles of copper and the yellow particles of sulphur lying side by side in the mixture.

Now heat the tube over a Bunsen's burner; the sulphur will

melt and get darker, but nothing further will happen until it begins to boil, when the mixture will suddenly glow brightly. Take the tube away from the lamp and observe that the glow continues, showing that heat is being evolved. Combination has, in fact, taken place; and after allowing the contents of the tube to cool, you will find that the sulphur and the copper have both disappeared, and a black substance (copper sulphide) is formed, which is composed of the two elements, but is wholly unlike them in appearance and properties. Detach a little of it from the tube, and prove its brittleness (unlike copper) by powdering it in the mortar.

It is to be noticed that the weights you have taken represent almost exactly one of the two proportions in which alone copper and sulphur will combine. The exact proportion is 63.5 parts by weight of copper and 32 parts by weight of sulphur. Another compound is known containing 127 (or twice 63.5) parts of copper to 32 parts of sulphur; but if you take weights of the substances in any other proportions, the excess of one or the other will remain uncombined.

This is an important characteristic of chemical combination; you may *mix* substances in any proportion whatever, but they will only *combine* in a few definite proportions.

B. ACTION OF COMPOUNDS ON ONE ANOTHER.

This may take place in more than one way.

1. The compound substances may combine with each other just as if they were elements.

A good example of this is afforded by the action of water upon quicklime (p. 66). The calcium oxide (quicklime) and the hydrogen oxide (water) combined to form the single substance calcium hydrate, while considerable heat was evolved.

2. They may undergo what is called 'double decomposition'; *i.e.*, they may decompose each other and exchange the elements (or groups of elements) which they contain.

This 'double decomposition' is a very common form of chemical action, and the following examples of it should be carefully studied.

EXAMPLES OF DOUBLE DECOMPOSITION.

1. Action between Potassium Iodide and Mercury Perchloride.

Weigh out 2 grms. of potassium iodide, and 3 grms.¹ of mercury perchloride; mix them together in a porcelain mortar, and grind them to powder.

As the grinding goes on, and the particles of the salts are brought closely into contact with each other, chemical action begins and the white mixture turns scarlet.

What has happened is this:—the potassium and mercury have changed places, the potassium combining with the chlorine and the mercury with the iodine; the latter compound forms a bright scarlet substance (mercury iodide); the same, in fact, which you formed in a recent experiment by direct synthesis.

The change may be conveniently represented thus:—

Before Decomposition.			After Decomposition.	
Substances taken.	Composition.		Substances obtained.	
Mercury perchloride, 271 parts.	{ Chlorine, Mercury,	71 parts 200 parts	{	Potassium chloride, 149 parts.
Potassium iodide, 332 parts.	{ Potassium, Iodine,	78 parts 254 parts		Mercury iodide, 454 parts.

Observe that we have here an example of both analysis and synthesis: some compounds being broken up, and others formed.

[Set aside the mixture in the mortar for use in the next Exercise.]

2. Action between Ammonium Chloride and Silver Nitrate.

The above examples have been selected to show the action

¹ These weights do not, as will be readily seen, represent the true proportions in which the substances act on each other. It is, however, found best to take a decided excess of the mercury salt; particularly for the purposes of the next exercise.

which occurs between *elements* whether isolated or in combination. But it is very often the case that *groups of elements* take part in a chemical action and are transferred from one compound to another just as if they were single elements. Such closely associated groups, as well as the elements themselves, are called '*radicles*,' as being the common root (*radicula*) or basis of a series of compounds.

Thus we find that the class of substances called '*NITRATES*' all contain nitrogen and oxygen associated in the proportion of 14 parts by weight of nitrogen to 48 parts by weight of oxygen. This group is called the '*NITRATE*' radicle.

Similarly the substances called '*AMMONIUM salts*' all contain nitrogen and hydrogen associated in the proportion of 14 parts of nitrogen to 4 parts of hydrogen. This group of elements is called the '*AMMONIUM*' radicle; and the elements thus connected may be transferred from one compound to another, apparently without losing their hold on one another.

The compounds formed by the union of two or more radicles, one being more electro-positive than the other (*i.e.* separated by electricity at the negative pole of a battery), are called '*Salts*' in the most general sense of the term.

Place in a test-tube 5 c.c. of solution of ammonium chloride (the ordinary laboratory solution), and add to it a few drops of solution of silver nitrate. A white substance insoluble in the liquid will appear, and on being shaken up will collect together in flakes and fall to the bottom, forming what is called a '*precipitate*.'

The action which has taken place may be thus represented:—

Before Decomposition.		After Decomposition.	
Substances taken.	Composition.	Substances obtained.	
Silver nitrate, 178 parts.	{ Nitrogen, 14 parts Oxygen, 48 parts Silver, 108 parts	{ Ammonium nitrate, 80 parts.	{ Silver chloride, 143.5 parts.
Ammonium chloride, 53.5 parts.	{ Nitrogen, 14 parts Hydrogen, 4 parts Chlorine, 35.5 parts		

Thus the compound radicles AMMONIUM and NITRATE com-

bine, forming a salt (ammonium nitrate), which is soluble in water, and therefore remains in the liquid; while the two simple radicles or elements SILVER and CHLORINE combine, forming an insoluble salt (silver chloride) which is precipitated as a white powder.

[If this is left in the light you will observe that it becomes darker in colour. This is a good example of the action of another Force, *viz.*, Light, in analysis; it has separated chlorine from the silver, leaving the latter either as subchloride or as metallic silver, forming a dark powder.

The whole art of Photography depends on this or similar chemical actions of light.]

DEFINITIONS.

The following definitions of terms illustrated in the foregoing experiments should be carefully remembered.

1. An **element** is a substance which has not, as yet, been separated into parts unlike itself and unlike each other.
2. A **compound** is a substance of definite composition which has been separated into two or more distinct elements.
3. A **radicle** is an element or a group of elements which can be transferred as a whole from one chemical combination to another.
4. A **salt** is a single substance produced by the combination of two or more radicles.

These radicles have, in many cases, not yet been isolated. No one, for example, has ever seen the ammonium radicle or the nitrate radicle. We can transfer them from one compound to another, but we have not been able to arrest them in their passage. They are like groups of figures in a money account, which have a definite value and may be transferred from the debtor to the creditor side without being actually exhibited in cash. The elements or 'simple radicles' may possibly be themselves compound, but even if their compound nature is discovered they will not cease to be radicles.

We may, then, define Chemistry to be

The study of the composition and properties of radicles, and of the ways in which they act on each other to produce substances permanently differing from themselves.

By doing so we shall have a description of the science which is independent of any possible modification of the atomic theory, and of any discovery of the compound nature of the so-called elements.

Additional Experiments.

Illustrations of the difference in the affinity of radicles for one another.

Two examples of this have already been given in the experiments on analysis by chemical affinity. Zinc was shown to displace hydrogen from its combination with chlorine, and also to displace copper from copper sulphate; proving that the affinity of zinc for the chlorine radicle and the sulphate radicle is greater than the affinity between these radicles and hydrogen¹. Similarly, other metals vary greatly in their affinities, and thus we are able to effect a regular series of replacements, as in the following example.

Replacement of copper by iron, mercury by copper, and silver by mercury.

1. Pour into a test-tube about 5 c.c. of solution of copper sulphate, and dip into it a strip of sheet-iron thoroughly cleaned with emery paper. The iron will soon be covered with a red film of metallic copper; the reason being that there is more affinity between iron and the sulphate radicle than between copper and that radicle. Hence the iron replaces the copper, iron sulphate being formed and copper separated in the metallic state.

2. Take out the iron, wash it with water from all traces of the solution, and put the copper-coated portion into a test-tube containing about 5 c.c. of solution of mercury perchloride. The copper will at once become coated with a bright metallic film of mercury (best

¹ Hydrogen is, in fact, more easily replaced than any other metal, and hence the salts formed by hydrogen with an electro-negative radicle, which constitute the so-called acids, for example, hydrogen chloride ('hydrochloric acid') and hydrogen sulphate ('sulphuric acid'), are constantly used to obtain other salts by the replacement of their hydrogen; as in the above instances, where zinc chloride and zinc sulphate were formed.

seen after rubbing the deposit with a cloth). Here the copper, from its strong affinity for chlorine, has displaced mercury; copper chloride being formed, and mercury separated.

3. Take the strip now coated with mercury, wash it with water and place upon it a drop of solution of silver nitrate, taken out of the bottle with a glass rod. A black deposit of metallic silver will be formed¹. The reason is that mercury, from its stronger affinity for the nitrate radicle, displaces the silver, mercury nitrate being formed and silver deposited.

[Another good example of replacement is given under LEAD (the 'lead tree').]

Influence of solubility, temperature, &c., on the action of chemical affinity.

It must not be supposed that the force of chemical affinity always acts in the same direction to form compounds. Much depends on the conditions under which it is allowed to act; the general rule being that a compound which, from its properties of insolubility, volatility, &c., is most disposed (under the conditions of the experiment) to separate from the rest, is formed, to the exclusion of others. The following examples will show what is meant.

Action between the radicles CALCIUM, AMMONIUM, CHLORIDE, CARBONATE, under different conditions.

1. Put 5 c.c. of solution of calcium chloride into a small porcelain dish, add an equal volume of solution of ammonium carbonate², and stir with a glass rod. A white precipitate, consisting of calcium carbonate, will be formed in such quantity that the mass will nearly become solid.

The reason is that, of the four radicles present, calcium and the carbonate radicle form a compound which (of all the possible combinations) is least soluble in water; and this is accordingly produced, while the ammonium radicle combines with chlorine to form ammonium chloride, which remains in solution.

[Express this reaction in your note-book in the form of a diagram, like those on pp. 84, 85.]

¹ The reason why the deposit has not the usual bright lustre of silver is that the particles, when thus thrown down, are so extremely small that they cannot reflect light (see also under SILVER).

² This quantity will, if the solutions are made of the strength directed in Appendix B, be more than sufficient to decompose all the calcium chloride: so that no soluble compound of calcium will remain in the mixture.

2. Now let us take the same four radicles and make them act under different conditions. Instead of taking them in solution at the usual temperature, let us bring them into contact in the solid state and at a high temperature.

Place the dish, containing the mixture of salts just obtained, on a sand-bath and evaporate the whole to dryness, stirring constantly to prevent portions of the solid being blown out of the dish by the formation of bubbles of steam below them. Then place the dish on a piece of wire gauze over an argand burner and heat the residue rather strongly. White fumes will soon appear which consist chiefly of ammonium carbonate, while a non-volatile residue will remain in the dish, which is found to consist (in great part, at any rate) of a salt of calcium soluble in water, *viz.* calcium chloride.

The fact is that, out of all the possible combinations of the four radicles present, ammonium carbonate is the most readily volatilised by heat. This compound is therefore formed, and the radicles, calcium and chlorine, combine to form the non-volatile residue. Observe, then, that by altering the conditions of chemical action we have just reversed the character of the chemical change, and re-formed the substances (calcium chloride and ammonium carbonate) with which we commenced.

[The presence of calcium chloride in the residue may be proved by mixing it with a little water, stirring the whole together, filtering it into a test-tube, and adding some solution of ammonium carbonate to the clear liquid. A white cloudiness will be formed, showing the presence, in the solution, of a compound of calcium soluble in water. If the residue had consisted of calcium carbonate, none of it would have been dissolved.]

EXERCISE 9.

Methods of washing Precipitates.

Apparatus required.—Porcelain mortar containing the mixture of mercury iodide and potassium chloride obtained in Experiment 1, p. 84; beaker; washing bottle with distilled water; funnel 8 cm. in diameter; filters 14 cm. in diameter; flask about 250 c.c. capacity; test-tubes and stand; glass rod; evaporating dish; solution of silver nitrate.

You obtained in the last Exercise (p. 84) a mixture of mercury iodide and potassium chloride. Since these substances are only mechanically mixed and not chemically

combined, and since one of them (potassium chloride) is very soluble in water, while the other (mercury iodide) is quite insoluble, the two salts can be readily and completely separated by adding water to the mixture in sufficient quantity to dissolve the potassium chloride, and then washing away by several changes of water all the solution from the insoluble residue of mercury iodide.

1. Washing a Precipitate by Decantation.

Add 50 c.c. of distilled water to the mixture in the mortar, and grind the whole with the pestle: then pour the contents



Fig. 63.

of the mortar into a beaker, rinsing out the last portions with a jet of water from the washing bottle. Leave it undisturbed for a few minutes that the precipitate may subside.

Meanwhile, fit a filter about 14 cm. in diameter, folded as already directed (p. 60) into a funnel about 7 or 8 cm. in diameter, taking care that the filter fits the funnel closely and does not project beyond its rim. Wet the filter with distilled water and allow it to drain for a few moments; then support the funnel in the neck of an empty flask (fig. 63), and pour the liquid from the beaker down the side of the filter, using a glass

rod to direct the stream, and taking care not to disturb the precipitate more than you can help. When the greater part of the liquid has been poured off, fill up the beaker again about two-thirds full of distilled water, stir up the precipitate with a glass rod¹, and leave it to subside (proceeding, meanwhile, with other work, such as the experiments with the mouth blow-pipe, given in the next Exercise). When the liquid above the precipitate is tolerably clear, pour it off again into the filter, still retaining the bulk of the precipitate in the beaker. Repeat this operation of filling the beaker with water, allowing the precipitate to subside, and then pouring off the clear liquid, two or three times. This process is called 'washing by decantation,' and is especially adapted for cases where we have a powdery, quickly-subsiding precipitate. Finally, after pouring off most of the water, transfer the whole of the precipitate to the filter by stirring it up with a little water, pouring it quickly into the filter, and again rinsing the beaker with more water. What has passed through the filter (technically called the 'filtrate') is, of course, a solution of potassium chloride, and need not be preserved.

It may happen that the first portions of the liquid which run through the filter are turbid. If this is the case, they should be poured back into the filter, another flask or beaker being placed to catch the fluid. If however the filtrate is still turbid, there is reason to suspect that there is a hole in the filter itself. In such a case it will be best to return the precipitate to the flask by making a large hole through the point of the filter, by means of a glass rod pressed vertically downwards, and washing down the precipitate by a strong stream of water from the washing bottle. Another filter should then be fitted to the funnel, and the precipitate transferred to it as before.

2. Washing a Precipitate on a Filter.

The washing of the precipitate must now be completed on the filter, in order to free it from all traces of the

¹ It will be found an advantage to fit upon the end of the glass rod a short ferule of india-rubber tubing, to avoid scratching or breaking the beaker while stirring.

solution of potassium chloride. This is done by pouring over it a gentle stream of water from the jet of the washing bottle, until the funnel is nearly, but not quite, full; the level of the water being on no account allowed to rise above the edge of the filter. When the washing water has entirely run through the filter (and not before), you may pour on a fresh supply, taking care to direct the stream on the sides of the filter, so as to wash the precipitate down towards the lowest point.

The precipitate must be washed in this way with several successive changes of water; in fact, until no potassium chloride can be detected in the filtrate. The presence of a chloride in a solution may be detected, as we have already seen (p. 75), by adding solution of silver nitrate, which gives a white precipitate. The filtrate should therefore be tested from time to time by allowing a little of it to run direct from the funnel into a test-tube and adding a drop of solution of silver nitrate. The cloudiness produced will get less and less on successive trials, and finally the filtrate will remain quite clear on addition of the test. When this is the case the mercury iodide may be considered sufficiently washed, and the funnel may be covered with a piece of paper turned down at the sides so as to form a cap, and put to dry (resting on its side in an evaporating dish) in a warm place. When dry, the mercury iodide may be detached from the filter, shaken into a short test-tube or small bottle, and kept (duly labelled) for use in a future exercise (see under MERCURY).

[Meanwhile it may be noticed that this substance when mixed with gum forms a splendid scarlet paint, the only drawback of which is its want of permanency. In illustration of this latter fact, the filter with the remains of the precipitate adhering to it, may be spread out flat on a piece of wire gauze and be heated gently over a lamp (care being taken not to breathe the vapour). The scarlet substance will be found to turn yellow, and at a slightly higher temperature, to volatilise. If the yellow residue is rubbed with a glass rod it will turn scarlet again.]

EXERCISE 10.

The Use of the Mouth Blowpipe.

Apparatus required.—Mouth blowpipe; blowpipe-burner on stand, fig. 6, p. 6; piece of platinum wire; piece of platinum foil; two or three pieces of charcoal; small glass mortar; watch-glasses; crucible tongs; test-tube; knife.

Sodium diborate ('borax'); sodium carbonate; potassium cyanide; strontium nitrate; solution of cobalt nitrate; manganese dioxide; tin dioxide; strong hydrogen chloride.

The mouth blowpipe consists, in its simplest form, of a tapering tube, usually bent near its smaller end to a right angle, and terminating in a fine jet. But as the moisture of the



Fig. 64.

breath soon collects in the tube and interrupts the flow of air, a much superior form of blowpipe is that which was introduced by Dr. Black, and which is represented in fig. 64.

All moisture is condensed in the wider part of the tube, while the movable nozzle can be readily unscrewed and cleaned out, if it should become stopped up by soot or oxide. Before the instrument is used, the nozzle should be carefully examined to see that the aperture is clear, round, and not very large, otherwise the cone of flame will be ragged, irregular, and brush-like.



Fig. 65.

The best fuel to be used with the blowpipe is undoubtedly ordinary coal-gas, where it can be obtained. The most efficient form of burner is that represented by fig. 65. It consists merely of a short piece of brass tube about 1 cm. in diameter, flattened out at one extremity until its edges form

a narrow rectangular aperture about 0.5 mm. broad, inclined at an angle of 70° to the axis of the tube.

• [If gas is not available, an oil lamp, a tallow lamp, or a spirit lamp fed with a mixture of ten parts spirit of wine and one part turpentine, may be used; or finally, but not preferably, a wax candle. The lamp should have a flat wick, which just before use must be carefully trimmed smooth and divided along the middle with the trimming scissors, so as to leave a furrow along which, and about 2 mm. above it, the blast of air from the blowpipe must be directed.]

Screw this burner into the same iron foot (fig. 6, p. 6) which serves as the base of the argand burner, and light the gas so as to get a flame about 5 cm. in height (about the size of an ordinary candle-flame). If the flame wavers, owing to draughts in the room, a screen of some kind must be arranged to protect it. Next examine the blowpipe-jet, and clean it out, if necessary, with a needle, until it deflects the flame into a steady pointed cone. Arrange the lamp at such a height that the hand which holds the substance in the flame may rest steadily on the table, while the other hand holding the blowpipe may also be firmly supported either on some part of the stand of the lamp itself or on a wooden block placed close to it. The blast of air should be directed obliquely downwards, parallel, in fact, with the orifice of the burner. The annexed figure (fig. 66, opposite page) will serve to make the position clear.

The first thing to be learnt in the use of the blowpipe is the method of keeping up a regular, continuous blast of air for several minutes without interrupting the ordinary process of respiration. This is by no means difficult. In the ordinary double organ bellows, we can distinguish two essential parts; (a) the lower compartment or 'feeder,' which by its alternate expansion and contraction supplies air intermittently; and (b) the upper compartment or 'reservoir,' which receives and stores up the air thrown in by the feeder, and sends it out in a continuous stream at a uniform pressure to the pipes. When the blowpipe is properly used, the lungs and the mouth are acting respectively as the feeder and the reservoir of the bellows; the

muscles of the cheeks acting as the weights placed on the reservoir to secure a constant pressure on the gas; the tongue, slightly drawn back and applied to the roof of the mouth, representing the valve between the feeder and the reservoir; and the nostrils representing the aperture through which air enters the feeder.

These analogies being borne in mind, the following general



Fig. 66.

directions will, it is hoped, be sufficient to guide the student in learning the use of the blowpipe; a few minutes' practice being of more value than a prolonged description.

Begin by distending the cheeks with air from the lungs; keep them thus distended while you breathe freely through the nose. In doing this you will have unconsciously placed the tongue in the position it should occupy as a valve between the

mouth and the lungs. Now insert the blowpipe between the lips, and expel the air from the mouth through the jet by compressing the muscles of the cheeks. When the stock of air in the mouth is nearly, but not quite, exhausted, introduce a fresh supply of air direct from the lungs, interrupting the ordinary respiration for a moment only, and slightly relaxing the muscles of the cheeks, so that they again become distended with air.

A difficulty will probably be found at first in keeping the pressure constant just at the moment at which air is thus thrown into the mouth from the lungs. A very little practice, however, will enable you almost unconsciously so to balance the action of the muscles of the chest and cheeks, that the latter yield exactly in proportion as the former impel air into the mouth, and thus no variation is perceptible in the blast of air from the jet.

When, after one or two trials, you find that you can produce a fairly uniform stream of air for a minute or so, you may bring the jet into the lamp-flame (which should be about as large as the flame of an ordinary candle) in the position above described, and use the blast of air to deflect the flame. The appearance of the latter (see fig. 67, p. 97) will sufficiently indicate the regularity and pressure of the stream of air. It should appear as a well-defined cone of blue light, burning noiselessly, surrounded by a faint nebulous yellowish envelope, which reaches for some distance beyond the apex of the cone. If it flickers, and burns with a roaring noise, either the jet is not introduced sufficiently far into the flame, or the aperture is too large, or the pressure of air too great. If it is irregular in outline, the aperture of the jet is not round, and must be cleaned out and rounded by introducing a large needle; or, if you are using a lamp with a wick, the latter may not be evenly trimmed, the projecting filament breaking the current of air. If the flame appears as a luminous tongue, either the aperture of the jet is too small, or the stream of air is not propelled with sufficient force; or, finally, the flame itself is too large.

The Structure of Flame.

Let us consider what is going on in the flame of a candle, or of gas burning at a jet, surrounded by air.

The wax-vapour as it rises from the wick, or the gas as it issues from the jet, mixes with the air; and when the temperature is sufficiently raised (by applying a burning match, for instance), the compounds of hydrogen with carbon, called 'hydrocarbons,' of which wax and coal-gas are chiefly composed, unite with the oxygen of the air, producing so much heat as to make them glow with that appearance which we call 'Flame.'

It is clear that the relative proportions of these hydrocarbons and air will be very different in different parts of the flame.

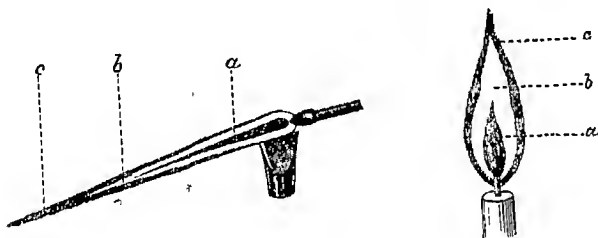


Fig. 67.

(a) Close to the jet, or the wick (a, fig. 67) the gas or wax-vapour will be in excess, since very little oxygen can reach this part, as will be presently seen. In this central portion, then, there can be no light-giving flame, but simply gaseous hydrocarbons strongly heated by contact with the hotter regions outside them.

(b) Farther off there will be a region (b, fig. 67) where the hydrocarbons and air are mixing in the proportions in which they will combine to form water and carbon dioxide, and here is the hottest part of the flame, because chemical combination is going on most fully and rapidly. It is also the most luminous part, since (as explained in reference to the Bunsen's burner, p. 4) oxygen is not supplied in sufficient quantity to

unite with the whole of the carbon as well as the whole of the hydrogen in the hydrocarbons; it therefore takes that for which it has most affinity, *viz.* the hydrogen, and leaves some (at any rate) of the carbon uncombined, as solid particles, which are raised to a glowing white heat by the temperature of combustion. This carbon is, however, itself burnt as it reaches the exterior of the flame.

(*c*) Farther off still, in fact quite outside the usually visible flame, there is a region (*c*, fig. 67) where there is a great excess of air strongly heated, but little or none of the hydrocarbons, because they will have been completely burnt before they reach this part.

The cone of flame produced by driving a stream of air from the blowpipe through a gas- or candle-flame (see fig. 67) is precisely similar in constitution to that above described; its structure and characters simply becoming more sharply defined and intensified by a judicious adjustment of the relative proportions of gas and air.

Uses of the different parts of the Blowpipe-flame.

1. The central portion, *a*, will take away oxygen from substances placed in it, *i.e.* will 'reduce' them; because it contains an excess of strongly heated compounds of carbon and hydrogen which have a great affinity for oxygen.

2. The intermediate region, *b*, will heat a substance most intensely; because it is the part where chemical combination between the hydrocarbons and the oxygen of the air is going on most abundantly and completely; and where, therefore, the temperature is highest.

3. The outer part of the flame, *c*, will add oxygen to substances placed in it, *i.e.* will 'oxidise' them; because it contains a large proportion of highly-heated air, the oxygen of which has its affinity for most substances greatly increased by an increase of temperature.

¹ Reduction in its usual sense means the taking away of oxygen from a substance, but in its most general sense it means the taking away from a salt some or all of the non-metallic radicle which it contains. A reference to various examples of reduction and oxidation will be found in the index.

These effects may be made much more decided by attending to the following rules:—

To expose a substance to the highest attainable temperature, it must be held at the point *b* in the figure, *i.e.* just at the tip of the blue cone mentioned above. Here the combustion is complete, and hence we have the maximum temperature which can be produced by the union of the gases.

To effect reduction;—more gas and less air will be needed; the object being to burn the gas only partially, and thus to compel it to obtain the oxygen necessary for combustion from the substance submitted to its action. Admit more gas, therefore, until the flame is about 7 cm. high, and, holding the blowpipe-jet at the *border* of the visible flame, blow a gentle stream of air through it, so as to deflect the flame in the form of a long luminous tongue, within the tip of which (between *a* and *b* in the figure) the substance to be reduced must be held, wholly immersed in the flame, and thus exposed to the same conditions as the ore in the body of a smelting furnace, surrounded by ignited fuel and combustible gases.


To effect oxidation;—more air and less gas is needed; the object being not only to burn the latter completely, but also to provide, over and above, a supply of highly heated oxygen, and thus to expose the substance to conditions similar to those which exist on the hearth of a cupelling furnace. Diminish the supply of gas until the flame is only about 4 cm. in height; introduce the blowpipe-jet about 1 mm. within the border of the flame, and blow more strongly so as to produce a well-defined blue cone, surrounded by a scarcely visible envelope; and hold the substance to be oxidised near the point marked *c* in the figure, about 1 cm. in front of the tip of the blue cone.

[It must be understood that, where an oil or spirit lamp is used, the raising and lowering the wick will have the same effect as increasing or diminishing the supply of gas to the burner.]

Examples illustrating the use of the Blowpipe-flame.

[A little of each of the substances required should be placed on watch-glasses or bits of writing-paper, near at hand.]

A. EFFECTS DUE TO ITS INTENSE HEAT.**1. Colours imparted to the flame by substances ignited in it.**

1. Take a piece of platinum wire about 8 cm. in length, and make a ring,  (actual size) at the end of it by bending it round the tip of the blowpipe-jet. Moisten it with a drop of distilled water, dip it into some sodium carbonate, and hold it in the hottest part of the blowpipe-flame. Notice the intense yellow colour imparted to the flame by the salt, which is highly characteristic of the metal sodium.

[The platinum wire must be made perfectly clean before being used for the next experiment. For this purpose, straighten out the loop, and wipe off the greater part of the salt with a wet cloth: then bend the end into a ring as before, dip it into a little strong hydrogen chloride placed in a watch-glass, and hold it in the hottest part of a Bunsen's burner-flame, until it ceases to impart any colour to the flame.]

2. Moisten the wire with strong hydrogen chloride, dip it into some powdered strontium nitrate, and hold it in the flame as before. The strontium present will impart to the flame a characteristic crimson colour.

[Other examples of the colours imparted to flame by substances will be found under the heads of BORATES, COPPER, BARIUM, and CALCIUM.]

2. Colours imparted to Borax by substances fused with it.

Heat the loop at the end of the platinum wire, and dip it into powdered sodium diborate (borax) placed in a watch-glass. A portion will adhere to the wire, and must be again brought into the blowpipe-flame. It will at first swell up and give off water, but will finally fuse into a colourless transparent

bead (of sodium metaborate), which undergoes no change on being further heated. More borax should be taken, if necessary, until a nearly round bead is obtained, filling up the whole of the wire ring. When the bead is cold, moisten it slightly with solution of cobalt nitrate, and again heat it slowly before the blowpipe, holding it in the hottest part of the flame, *i. e.* at the point of the blue cone. When all action appears to have ceased and the bead is as clear as at first, withdraw it from the flame and allow it to cool. It will now be seen to have acquired a deep blue colour, if the cobalt salt has been taken in the right proportion. If the bead appears nearly black, too much of the cobalt nitrate has been added, and the wire after being again heated must be tapped on the edge of a plate, so as to shake off the greater part of the still fluid bead, then dipped into the borax and again heated before the blowpipe. If the blue colour is very faint, a little more of the cobalt nitrate must be taken; but the delicacy of the reaction is so great that it is hardly possible to take too little of the substance.

[To clean the wire, heat the bead strongly till it melts, and immediately shake it sharply off into the sink or upon a plate: melt some more borax upon the wire, and shake the bead off in the same way. On again making a bead, it will be usually found sufficiently colourless for other experiments.]

[Other examples of the use of the blowpipe in simple ignitions will be found under the heads of SILICATES, CHROMIUM, and ALUMINIUM.]

B. EFFECTS OF OXIDATION AND REDUCTION.

[In the preceding experiment it is immaterial into what part of the flame the substance is introduced, since the colour imparted to borax glass by cobalt is the same whether the oxidising or reducing flame be employed to melt the bead. In the following experiments, however, the distinction between the two flames must be carefully observed, and the substance should be kept steadily for at least half a minute in the one or the other flame, as directed.]

1. Oxidation and reduction in a borax bead.

Form a clear colourless borax bead as above directed; add

to it a very small particle of manganese dioxide, and heat it, first at the hottest part or tip of the flame until the substance has dissolved in the borax, and then in the oxidising flame, holding it at least 1 cm. in front of the visible flame. The bead will acquire an amethyst colour. Now heat it again, but this time in the reducing flame, holding it so that the luminous portion shall completely envelope it, and taking care that it does not, even for a moment, remain in the outer border of the flame. It will eventually be found that the amethyst colour has nearly or completely disappeared, and the bead is as colourless as at first. But if it be again held in the oxidising flame, the colour will return.

The reason is this,—Manganese unites with sodium borate to form two distinct compounds, one containing more oxygen than the other. That which contains most oxygen is deeply coloured: the other is colourless. By heating the substance in the oxidising flame, we determine the formation of the first, or highly oxidised salt; but when this is transferred to the reducing flame, oxygen is taken away from it and the colourless salt is formed.

2. Reduction on Charcoal.

[For such experiments as the following, small flat blocks of charcoal are required, which should be carefully selected free from cracks and of close even texture. Good pieces may always be found among ordinary charcoal, sold for burning, and should be cut across the grain with a fine saw into pieces about 2.5 cm. thick, and 3 or 4 cm. in diameter. A cross section is

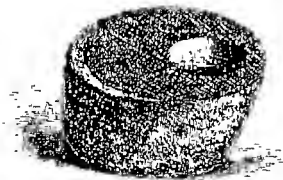


Fig. 68.

always to be preferred to a longitudinal one, since the former absorbs the flux more readily, and does not split when heated.]

Select a piece of charcoal with a flat surface, and cut a small conical cavity in it with the point of a knife or spatula, as shown in fig. 68, so as to form a small crucible for containing

the substance; taking care that the surface of the charcoal extends some little way beyond the hole, so that any incrustation may be retained for examination. The charcoal may be conveniently held in a pair of crucible tongs, their bent points being turned upwards, as in fig. 66, p. 95.

Mix together in a small glass mortar a little tin dioxide (about as much as will lie on the end of a spatula) and twice as much potassium cyanide¹; then fill the cavity in the charcoal with the mixture, taking care not to scatter any over the surface of the block. Bring the mixture into the reducing flame of the blowpipe, holding the charcoal in the crucible tongs, as shown in fig. 66, p. 95, slightly inclined towards the jet, so that the flame may play directly into the hole. The mass will readily melt, and bright globules of metallic tin will make their appearance, while the salt will be gradually absorbed by the charcoal. Maintain the heat steadily until the scattered particles of metal have run together into one globule, and the flux (see note below) has disappeared; then withdraw it quickly from the flame and let it cool. Try the malleability of the metal by detaching it with a knife from the charcoal, placing it in a strong porcelain mortar and pressing the pestle strongly down upon it. It will be found to spread out under the pestle into a flat plate, not crumbling to powder or even tearing at the edges.

3. Oxidation of reduced metal.

Make a hole in another part of the charcoal support, and place in it the piece of tin which you have just obtained. Fuse it in the reducing flame, and notice that its surface can be kept quite bright so long as it is held in that flame. Remove it into the oxidising flame, lowering the gas flame and slightly increasing the blast of air. It will now become tarnished, a crust of white oxide being formed, which appears to grow

¹ The action of this salt will be found fully explained under CYANIDES. It will be sufficient to say here that it acts, (1) from its affinity for oxygen, as a reducing agent; (2) from its easy fusibility in forming a coating over the globules of reduced metal, to protect them from the action of the oxygen of the air. Such a substance is called a 'flux.'

out of the metal. Bring it again into the reducing flame, and a bright globule of metal will be again formed. The reduction should be assisted by the addition of a minute quantity of potassium cyanide, to act as a flux.

[Other examples of oxidation and reduction by the blowpipe-flame will be found under the heads of COPPER, IRON (borax-beads), LEAD, and CADMIUM (reductions on charcoal).]

[The pieces of platinum wire for blowpipe use may be conveniently preserved in the following way :—

Fit a cork to a wide-mouthed 1 oz. bottle ; then with a sharp cork-borer cut two or more holes in the cork, about 5 mm. in diameter. Push out of the borer the small cylinders of cork extracted from the holes, and make a pin-hole along the axis of each. Pass one end of the piece of platinum wire through the pin-hole and bend it into a hook on the other side of the cork to secure the wire in its place. Lastly, fill the bottle nearly to the neck with dilute hydrogen chloride; cork it, and fit into each hole a cork cylinder with wire attached, so

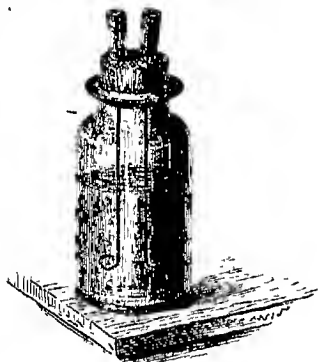


Fig. 69.

that the end of the wire may be immersed in the dilute acid. By this means the wires will be kept always clean and ready for use ; while the cork cylinders will serve as convenient handles and prevent the wires from being lost. Fig. 69 represents a bottle thus fitted.]

EXERCISE 11.

The general properties of Gases, and the modes of collecting them.

Apparatus required.—Pneumatic trough (fig. 1, p. 2); two cylindrical gas jars, 5×20 cm.; one ditto, 3×10 cm.; small wide-mouthed gas bottle, holding about 200 c.c.; elbow-tube with long branch, fig. 33, p. 32; retort-stand; test-tubes; tube measure, fig. 48, p. 49; pipette; corks; cork borers; india-rubber rings; piece of india-rubber tubing (small size) about 40 cm. long.

Most of the substances to be dealt with in the earlier Exercises in Sect. II. are gases; and in order to avoid waste and loss of a substance which may have given some trouble to prepare, it will be useful to examine such properties as belong more or less to all substances in the gaseous state.

In the first place it is observed that all gases mix rather quickly with each other, when brought into contact. This property is called 'Diffusion;' and the lighter a gas is, the more quickly it diffuses into other gases. Coal-gas, for instance, if allowed to escape from a pipe, is soon discernible by its smell in every part of a room or house. Hence in dealing with any gas, if we wish to keep it pure we must separate it from the air or other gases by confining it in a well-closed bottle or jar; and in transferring it to other jars or bottles we must make it pass in bubbles through some liquid on which it has no action. For such purposes the pneumatic trough, filled with water or mercury, is generally used; although some gases may be dealt with by the rougher but readier method of displacement.

A. Collection and decantation of gases over the pneumatic trough.

1. Fill the trough with clean water up to the level of the overflow-pipe, or about 2 cm. above the shelf, and place it before you on the table, the broad fixed ledge being farthest

from you, and the movable shelf being placed near the left-hand end of the trough. If the small side trough (the end of which is shown at *b*, fig. 1, p. 2) is provided, it should be placed below the ledge so as to catch any water which overflows through the tube at the corner *a*. Take one of the large cylindrical jars, and, holding it nearly horizontally in the right hand, plunge it into the water, the mouth of the jar being held a little higher than the closed end, in order that the air may more readily escape. When the jar is filled with water and wholly immersed in the trough, bring the closed end uppermost and raise the jar vertically until its mouth is on a level with the shelf, and then move it laterally until it rests over the hole in the shelf: taking care to keep the mouth always below the surface of the water. So long as this condition is fulfilled, you will find that the jar remains full of water, the column of water being retained in it by the pressure of the air on the surrounding water. Next, attach a piece of india-rubber tubing to the short branch of an elbow-tube and bring the other end of the elbow-tube just under the hole in the shelf. If air is then blown from the mouth through the tube, it will rise in bubbles to the top of the jar, displacing the heavier water. This illustrates the way in which all gases which have no action on water may be collected.

2. Slide the jar, now filled with air, to the side shelf of the trough, taking care to keep its mouth below water. Fill another similar jar with water as above directed, and place it over the hole in the shelf. The air in the first jar has now to be transferred or 'decanted' into this latter jar in a manner quite analogous to that in which we pour water from one vessel to another, only that instead of pouring water downwards through air, we have to pour air upwards through water. Hold the jar containing water steady with the left hand, bring the mouth of the other jar under the hole in the shelf, and gradually depress its closed end so that the air contained in it may ascend bubble by bubble through the hole into the jar placed over it. The level of the water in the latter will fall until the jar is completely filled with air. (The reason for steadying it with the left hand

will now be evident, since it will show a tendency to topple over, owing to the upward pressure of the water; and it is best never to fill a jar completely with gas, but only so far that the level of the water inside and outside the jar may be the same. It can easily be filled completely, when required, from another jar.)

Repeat the experiment, decanting air from the one jar into the other until you can do so without allowing a single bubble to escape. It is not necessary that the jar should rest on the shelf, but it may be held in the left hand, as in fig. 73, p. 130, its mouth being retained about 2 cm. below the water-level, and the mouth of the jar of air brought close to its edge, and a very little to the right of it, since the bubbles of gas have a forward as well as an upward direction.

3. You may, in the next place, fill the small jar with air and decant its contents into the larger one. Then try to decant the air back from the large jar into the small one. This will not be found so easy, since the bubbles of air from the mouth of the jar are so large that unless the jars are held steady and the decantation is very gradual a waste of gas is likely to occur, and must occur if the disproportion between the mouths of the jars is very great. You will know that none has been lost if the small jar is just filled with the air decanted from the larger one.

[When gas is to be transferred from a large jar to a test-tube, it is better to decant it first into a jar of intermediate size, and then into the tube; or the object may be effected in the following way. Fill the tube in the usual way with water, and insert into its mouth, still held downwards below the water-level, the up-turned beak of an inverted funnel about $\frac{1}{4}$ cm. in diameter. Retain the funnel in its position by placing the little finger under the rim, the tube being held upright between the thumb and the other fingers. If, now, air be decanted from a larger jar, bubble by bubble, into the funnel, the bubbles will rise into the tube without any loss, the displaced water making its escape between the mouth of the tube and the funnel, which latter should not be held too closely in contact with the tube.]

B. Collection of gases by displacement.

This is a method of collection which depends upon the difference between the density of a gas and that of common air. It is especially useful in cases where the gas to be collected is so soluble in water that it would be impracticable to collect it over that fluid. In such cases a trough filled with mercury might be used, but the great expense of this would place it beyond the reach of most of those for whom these exercises are intended.

When we pour water into a vessel, the water, being heavier than the air contained in the vessel, descends to the bottom and displaces the air, which is driven out at the top. Precisely the same thing occurs when we lead a gas heavier than air into an open jar. The gas does not mix with the air at once, but collects at the bottom of the jar and gradually rises, driving the air before it, and finally overflowing the edge of the jar like other fluids. It is obvious that a gas lighter than air may be similarly collected by simply reversing the position of the receiving vessel, placing its mouth downwards, and leading the gas into its upper part; as may be illustrated in the following way with coal-gas¹.

Place a small wide-mouthed gas bottle (the stopper being removed), inverted, upon the smallest ring of the retort-stand, and put round it one of the larger retort-rings in order to steady it (as in fig. 76, p. 148). Connect the short branch of an elbow-tube by an india-rubber tube with the gas supply, and pass up the long branch as high as possible within the bottle. Turn on the gas partially, so that a moderate stream may flow into the bottle, where, being lighter than air, it will collect in the uppermost part, displacing the air, which will escape at the mouth of the bottle. In about 10 seconds (or the time taken to count '20' deliberately) turn off the gas and withdraw the

¹ If coal-gas is not at hand, a little hydrogen may be made in a test-tube by acting on dilute hydrogen chloride with zinc as directed in expt. (a) p. 80; the mouth of the test-tube being passed up into the inverted bottle.

tube: then bring a lighted match to the mouth of the bottle, when the gas will show its presence by taking fire. Observe that it does so before the light comes *within* the mouth of the bottle, showing how quickly it is diffusing into the air. Air is, of course, diffusing into the bottle at the same time; and, in fact, it is not easy to obtain a perfectly pure gas by collection in this way.

In collecting gases by displacement, the following rules should be attended to.

1. Pass into the jar at least twice the volume of gas required to fill it; since diffusion must take place between the fluids with greater rapidity in proportion as their densities are less, and hence the boundary-line between the gas and air is never so sharply marked as in the case of water and air.

2. All currents of air in the room must be avoided as much as possible; the tendency of such currents being to stir up the gas, and produce a more rapid mixture with air than diffusion alone would cause.

Additional Experiments.

A. Effect of change of temperature on the volume of a gas.

Take a test-tube about 2.5 cm. in diameter and 15 or 20 cm. in length; place round it, about the middle, a small india-rubber band; fill it with water, and place it inverted upon the shelf of the trough. Decant air into it from a small test-tube until, when your eye is brought on a level with the india-rubber ring, the lowest part of the curve which is formed by the surface of the liquid appears *just* to touch the upper edge of the ring (see p. 49, note). Heat some water in a test-tube nearly to boiling, and pour it over the tube containing the measured volume of air. The surface of the water in the tube will rapidly sink below the ring, showing that the air has expanded with the heat; but when a little water at the ordinary temperature is poured over the tube, the air will contract to its original volume. If you can obtain any ice or snow, you may place some in a flask and add some water; when the latter has been cooled down nearly to the freezing-point it should be poured over the tube containing the air. The surface of the liquid will now rise above the ring, the air contracting in volume as the temperature is lowered.

Try a similar experiment with coal-gas, decanting the requisite

quantity into the tube from an india-rubber tube connected with the gas supply.

The same experiment might be tried with any other gas, and you would find it to be a universal law that *the volume of a gas increases as its temperature is raised, and decreases as the temperature is lowered.*

Exact determinations of the amount of this variation in volume were first made by Gay Lussac, who established the following law, applicable to all true gases, whatever their nature, —

FOR EVERY CHANGE IN TEMPERATURE OF 1°C . A GAS CHANGES IN VOLUME BY $\frac{1}{273}$ ($=0.00366$) OF THE VOLUME IT OCCUPIES AT 0°C .

B. Effect of change of pressure on the volume of a gas.

Since gases are ordinarily measured under the pressure of the atmosphere, it will be most convenient to vary the pressure on the gas which is being examined, by adding to, or taking from, the atmospheric pressure. For this purpose a column of water or mercury may be employed in the following way.

Fit a good cork to the tube-measure already made (or any stout test-tube about the same size); bore a hole in it, and fit into the hole a straight piece of glass tubing about 20 cm. in length, and 6 or 7 mm. in diameter (the pipette you have made (p. 33) will do very well). Take out this tube, when fitted, and insert the cork tightly into the test-tube. Slip over the small tube a narrow india-rubber ring (cut from a piece of tubing), and sink it vertically in the trough almost to the bottom; then, holding the test-tube by the rim (lest the warmth of the hand should alter the volume of the enclosed air), fit the small tube into the cork, raise or lower the apparatus until the level of the water in the tube and in the trough is the same, and adjust the ring to this level. The air enclosed in the tube is now at the same pressure as the external air; since the columns of water inside and outside the tube, being of the same height, just balance each other, and thus the pressure of the external air is transmitted by the water to the air within the tube without gain or loss. Slip under the extremity of the tube one of the larger gas jars, wholly immersed in the trough, and raise the whole out of the trough, the gas jar serving as a deep pneumatic trough. It will now be possible to vary the pressure on the air enclosed in the test-tube by simply raising or lowering the tube in the jar of water; and owing to the difference in capacity between the test-

tube and the small tube connected with it, a slight alteration in the volume of the air in the former will cause a very decided change in the level of the water in the small tube.

1. Effect of diminishing the pressure.

Set the jar on the table, and raise the tube until its extremity is only just below the water-level: you will observe that the water in the tube falls below its former level, showing that the volume of the air in the apparatus has increased. This enclosed air is obviously under *less* than the whole pressure of the external air, since the pressure of the latter is partly balanced by the column of water in the tube standing above the level of the water in the jar.

Therefore you learn that *diminution* of pressure causes an increase in the volume of a gas.

2. Effect of increasing the pressure.

Next, sink the tube in the jar until it touches the bottom: the water will rise above its original level in the tube, showing that the enclosed air has contracted in volume. This air is now exposed to a pressure *greater* than that of the external air, the latter being aided by the column of water in the jar which is above the level of the water in the tube.

We have thus obtained evidence that *increase* of pressure causes a diminution in the volume of a gas¹.

By exact experiments of the above kind, in which the volumes occupied by a portion of a gas under the pressure of columns of mercury of different known lengths were measured, the following law, applicable to all gases, was established by Mariotte (and Boyle),—

THE VOLUME OF A GAS VARIES INVERSELY WITH THE PRESSURE UPON IT.

Thus, for example, taking 100 c.c. of a gas under the ordinary atmospheric pressure,—if we put twice the pressure upon it, it contracts to half the volume, *i.e.* becomes 50 c.c.;—if we put half the pressure upon it, it expands to twice the volume, *i.e.* becomes 200 c.c.

¹ Much greater variations in pressure can be obtained by connecting the end of the tube with a funnel by means of a long india-rubber tube; both this and the funnel being filled with water by immersing them in the trough (care should be taken to get rid of all air-bubbles). If the funnel is then raised or lowered, the column of water in the tube is added to or subtracted from the pressure of the air, as above explained.

It may be convenient to note that a column of water 1 metre in height very nearly = $\frac{1}{10}$ of the average air-pressure.

The practical lesson to be learnt from these experiments is that in measuring gases over the pneumatic trough especial care must be taken to deal with them under equal conditions of temperature and pressure (or to make allowance for any difference): otherwise the apparent volumes will not represent the real quantities we wish to take. The jars should not be held more than is necessary in the warm hands, and the volumes should be read with the water as nearly as possible at the same level inside and outside the jar.

SECTION II.

PREPARATION AND EXAMINATION OF THE PROPERTIES
OF THE PRINCIPAL NON-METALLIC RADICLES
AND THEIR COMPOUNDS.

[An asterisk is prefixed to those experiments which illustrate properties of the substance which are considered especially applicable for its detection in the course of qualitative analysis.]

1. OXYGEN AND ITS COMPOUNDS.

[Symbol of oxygen-atom ¹ ,	O
Weight " "	16 hydrogen-atoms.
Formula of oxygen-molecule,	O ₂
Weight " "	32 hydrogen-atoms.]

Apparatus required.—Pneumatic trough; argand burner; fish-tail burner, or spirit lamp; Bunsen's burner; Bunsen's holder; retort-stand; sand-bath; piece of wire-gauze; corks; cork-borers; rat-tail file; three-square file; Florence flask (fig. 15, p. 10); test-tube about 1.5 cm. in diameter; glass tubing, about 5 mm. in external diameter; porcelain mortar; two small porcelain dishes; scales and weights; *deflagrating jar*; *deflagrating cup*; one wide-mouthed stoppered bottle, holding about 700 c.c.; two ditto, holding about 200 c.c.; two cylindrical gas jars, 20 × 5 cm.; ground-glass disc, 8 cm. in diameter; taper on wire (fig. 12, p. 8); cedar spills; box of test-papers; sheets of writing-paper

Potassium chlorate; manganese dioxide; clean sand; sulphur; piece of fine watch-spring or steel wire; piece of magnesium ribbon, 10 cm. long; German tinder, or fusee.

Oxygen is generally obtained by the action of heat on some compound containing it. Thus when mercury oxide was heated (p. 77) it was found to give off oxygen; and this

¹ A short explanation of these symbols, &c., is given in Appendix D. Those, however, who are only just commencing chemical work will find it best to defer the study of them until the series of nitrogen oxides has been examined.

method's of interest as being the one used by Priestley in his discovery of oxygen. But practically another substance, potassium chlorate, is nearly always used in the preparation of the gas. This salt contains potassium, chlorine, and oxygen, and when it is heated the whole of the oxygen in it (about one-third of its weight) is evolved, and a compound of potassium with chlorine (potassium chloride) remains. This may be tried on a small scale as follows.

Place a few crystals of potassium chlorate in a dry test-tube, supported in a slanting position in a Bunsen's holder (as in fig. 62, p. 77), and apply heat. The salt will fuse into a liquid, and at a temperature just above its melting-point, will give off a gas with effervescence, which may be shown to be oxygen by its power of rekindling a glowing splinter of wood, such as a cedar spill, introduced into the tube. Continue heating the salt for half a minute, then remove the lamp, and when the fused mass in the tube is cool, pour in a little water, shake it up with the residue, and test the solution with a drop of silver nitrate. A white precipitate will be produced, which we have seen already (p. 75) to indicate the presence of a chloride¹.

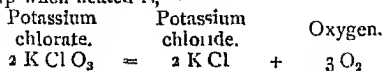
[The reaction may be expressed as follows²:—

Substance taken.	Composition.	Substances obtained.
Potassium chlorate, 122.5 parts by weight.	<div style="display: inline-block; vertical-align: middle;"> <div style="font-size: 3em; vertical-align: middle; margin-right: 0.5em;">{</div> <div style="display: inline-block; vertical-align: middle;"> Potassium, 39 parts — Chlorine, 35.5 parts — Oxygen, 48 parts — </div> </div>	<div style="display: inline-block; vertical-align: middle;"> <div style="font-size: 3em; vertical-align: middle; margin-right: 0.5em;">}</div> <div style="display: inline-block; vertical-align: middle;"> Potassium chloride, 74.5 parts. Oxygen, 48 parts.] </div> </div>

¹ Chlorates themselves do not give any precipitate when tested thus, as will be proved in a later exercise, when their properties are more fully examined.

² The student is advised to write out all the chemical actions which he meets with, in some such form as the above. When he has studied the properties and combinations of two or three of the elements he will be better able to appreciate the grounds of the atomic theory, and the system of symbols by which all chemical changes may be concisely yet fully expressed in the form of equations, as explained in Appendix D.

The equation expressing the mode in which molecules of potassium chlorate break up when heated is,—



A very pure gas may be obtained by this method, but the temperature at which the decomposition takes place is so high that ordinary glass flasks cannot support it without softening. It is found, however, that if the salt be mixed with manganese dioxide, the decomposition takes place at a much lower temperature, and with greater rapidity. The manganese dioxide does not, apparently, give up any of the oxygen which it contains: at any rate, it is found at the close of the action to be unaltered in composition, and may be employed repeatedly with fresh portions of potassium chlorate.

Preparation of Oxygen gas.

In the first place the materials for the preparation of the gas should be got ready, as it is important that they should have time to dry thoroughly. If this precaution be neglected the flask in which they are to be heated is not unlikely to crack during the experiment, owing to the moisture condensing in the neck and dropping down upon the hotter portions of the glass.

Weigh out on paper (as directed in Sect. I, Exercise 5, p. 59) 25 grms. of crystallised potassium chlorate; reduce the crystals to powder in a mortar; then place the salt in a porcelain dish or the sand-bath to dry.

Weigh out, similarly, 6 grms. of manganese dioxide, and place it in another porcelain dish on the sand-bath near the potassium chlorate, stirring them both occasionally with a glass rod.

In the next place, you have to prepare an apparatus for generating and collecting the gas. Since heat is required to decompose the potassium chlorate, a flask supported in a retort-stand will serve to contain the materials; and since oxygen gas is scarcely soluble in water, it may be collected over the pneumatic trough filled with water; a bent glass tube will serve to convey the gas from the flask to the trough.

Take a clean Florence oil-flask, selecting one which has a smooth even mouth; roughen the sharp edges of the mouth with a file; or, if a Herapath's blowpipe is at hand, turn the

edges outwards so as to form a spreading lip, as directed, p. 45. Cut off a piece of the glass tubing about 65 cm. in length, and round the edges in the usual way: then (using the fish-tail burner) bend the tube to an acute angle, making the middle of the bend not more than 8 cm. from one extremity; and lastly make a slight bend in the opposite direction as near the other extremity as possible, so as to give the tube the shape shown in fig. 70. The object of this second bend is to facilitate the escape of the bubbles of gas by giving them a forward and upward direction.

It may be found convenient to use a cork handle (p. 32), in case the end of the tube should become too hot to be held in the fingers. When the glass is quite soft, hold the tube out



Fig. 70.

in front of you, so that the eye may be in the plane of the first bend; it will then be easy to turn up the end which is nearest to you, so that both the bends may lie in the same plane but in opposite directions.

Next, choose a sound cork very slightly larger than the neck of the flask, squeeze it until it becomes soft and elastic, and bore a hole through it for the delivery tube, using a cork-borer which is rather smaller than the glass tubing which you have used.

The end *a* should now be fitted with gentle pressure and twisting motion into the cork, through which it should pass completely and project slightly at the opposite end. Do not attempt to use much force in pushing the tube into the cork, or you may break the tube and be cut with the splinters of glass; but enlarge the hole with the rat-tail file, until the tube will enter it without much difficulty.

The potassium chlorate and manganese dioxide may now be taken from the sand-bath, and set aside to cool for a minute

or two, during which time the pneumatic trough may be filled with water up to a level about 2 cm. above the shelf. It is well to have a jug of water at hand, in case more should be wanted. Take the deflagrating jar, slightly grease the stopper and fit it tightly in its place; then immerse the jar sideways in the water, raising the open end a little, so as to allow all the air to escape. When the last bubble is gone, depress the open end and raise the jar by its neck (taking care to keep the lower end below the water-level), until it can be moved laterally to its place on the shelf. Fill the two cylindrical jars with water and place them inverted on the shelf. The large bottle should be filled with water from a jug, the (greased) stopper inserted quite loosely and held in its place with one hand, while with the other the bottle is inverted, and its mouth brought below the level of the water in the trough, when the stopper may be withdrawn, and the bottle moved to the shelf. It is a good plan to keep the stopper upon the bottle, when thus inverted, in order to prevent its being mislaid.

[Besides the above jars and bottle, two small gas bottles should be filled with oxygen and reserved for use in future Exercises; unless, as is the case in many laboratories, a supply can be obtained from a gas-holder, whenever wanted. These bottles may, after being filled with water, be placed near at hand and not brought into the pneumatic trough until required for filling, in order to avoid overcrowding the shelf.]

Now mix the potassium chlorate and manganese dioxide in the mortar with a few circular strokes of the pestle, add to the mixture an equal bulk (not more) of fine dry sand¹, and grind the whole until thoroughly mixed; then shake it out on a sheet

¹ Unless this addition of sand is made, it often happens, especially if there is rather more than the due proportion of manganese dioxide in the mixture, that there is a sudden rush of gas at the last, a low incandescence spreading through the half-fused mass. It is well to be prepared for this, and to take away the lamp at the moment when you perceive any tendency to a rush of gas. Of course the only possible risk would arise from the delivery tube not being sufficiently large to carry off the rapid current of gas, or becoming obstructed by particles of the mixture mechanically carried over with the gas. When sand is added, however, as above directed, the decomposition proceeds with perfect regularity from beginning to end, and much less attention to the lamp is required.

of paper, and transfer it to the flask. After wiping the neck of the latter, fit the cork with the bent delivery tube into its place, with careful pressure (grasping the flask by the neck, not the bottom, lest it should break and cause a serious wound), and support the flask on a piece of wire-gauze bent into a shallow cup, and resting on the largest ring of the retort-stand. The smallest ring should be passed over the neck of the flask to secure it in an upright position, and the latter should be fixed

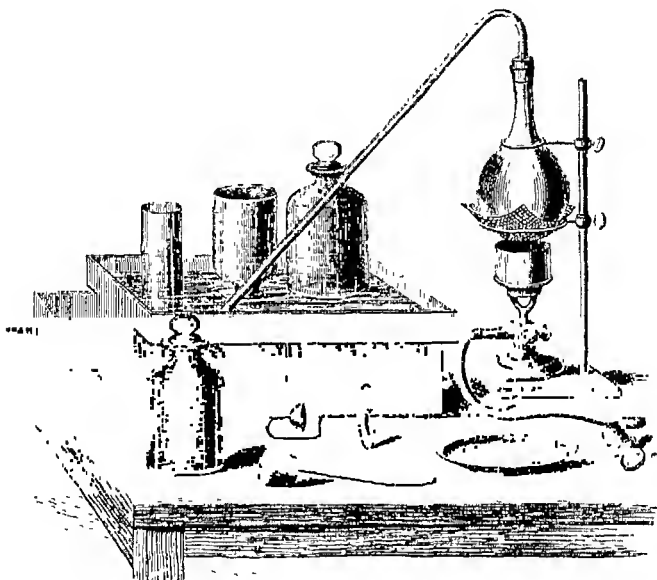


Fig. 71.

at such a height that a lamp may be easily placed beneath it, and that the end of the delivery tube may pass under the shelf of the pneumatic trough, and be about 3 or 4 cm. below the surface of the water. The whole apparatus will then be arranged as shown in fig. 71.

Before beginning to heat the mixture in the flask, you should ascertain whether there is any leakage owing to the cork being unsound or badly fitted. Place the warm hand on the flask for a few seconds, and observe whether, owing to the expansion

by heat of the air in the flask, the level of the water in the delivery tube is depressed below the level of the water in the trough, and finally a bubble or two of air escapes, and also, whether on removal of the hand the water only returns *by degrees*, as the air cools, to its original level in the tube. If no depression of the level takes place, it shows that some air must escape through a leak in the cork-joint, which must be stopped before anything further is done. If the fault is not cured by pressing the cork farther into the neck of the flask, it will generally be best to take a new cork altogether.

When you have proved that the apparatus is air-tight, you may proceed to heat the flask by a gas or spirit lamp. The best form of gas lamp for the purpose is an argand burner (or other form of ring burner), since it distributes the heat over a larger surface, and can be made to give a very small flame if required.

The first effect of the heat (which should be applied cautiously and gradually) will be to expand the air in the flask, which will escape in bubbles through the water in the trough.

In a short time the stream of bubbles, which had slackened, will become more rapid, showing that gas is being evolved from the mixture. As soon as this takes place, slide one of the cylindrical jars along the shelf until its mouth is over the hole and the bubbles can rise freely into it. The heat must be carefully regulated, so as to keep up a moderately rapid stream of bubbles. It will be scarcely worth while to test the first jarful of gas, which will certainly be mixed with air. Fill the jar again with water, and place it as before to receive the gas. When it is full, slide it off the shelf with one hand, and with the other bring a ground-glass plate upon its mouth, while under water; raise the jar out of the water, still keeping the glass plate pressed against its mouth, and place it mouth upwards on the table. Now light a cedar spill at the lamp, blow it out, and, while its end is still glowing, plunge it into the jar of gas. If it is rekindled, bursting sharply into flame, the gas is sufficiently pure for experiments. If this is not the case, return the jar

at once to the trough, fill it again with gas, and test it in the same way.

When you have thus ascertained that the gas is pure, you may proceed to fill the jars and bottles with it, bringing each in succession over the hole in the shelf, and when it is full of gas sliding it (without raising its mouth above the level of the water) to one end of the shelf, and bringing another into its place¹. When the deflagrating jar has been filled, slip under its mouth a shallow tray (a common plate or saucer will answer the purpose); then, keeping the tray horizontal and the mouth of the jar resting in it, raise both out of the water and place them on the table. The water remaining in the plate will thus act as a valve to prevent the gas in the jar from escaping. The cylindrical jars may be left on the shelf till required.

As soon as the jars and bottles are filled with oxygen, take out the cork from the flask, and raise the delivery tube at once out of the water; then (and not till then) withdraw the lamp, and set the flask aside to cool.

[The porous, half-melted mass which it contains may be readily washed out by a little warm water. It consists of a mixture of potassium chloride, manganese dioxide, and sand, and will not be worth preserving. The flask will be found scarcely, if at all, injured, and after being cleaned and dried is fit for use again.]

¹ While the jars are being filled you may calculate the quantity of oxygen obtainable from the 25 grms. of potassium chlorate you have taken. It is known (see the diagram on p. 114) that 122.5 parts by weight of the salt yield 48 parts by weight of oxygen; and the 25 grms. must yield the same proportionate weight of the gas. It is, then, only necessary to work out the following proportion sum,—

Parts by wt. of pot. chlorate.	Parts by wt. of oxygen yielded.	Wt. of pot. chlorate taken.	Wt. of oxygen obtained.
122.5	48	25 grms.	x

The fourth term (which need only be calculated to two decimal places) will give the *weight* of the oxygen; and in order to ascertain how many litres this will measure, it is sufficient to know that 1.4 grms. of oxygen measure 1 litre (nearly). Thus you have to find out how many times 1.4 grms. are contained in the whole weight of oxygen, *i.e.* to divide this weight by 1.4; and the quotient will be the number of litres of oxygen obtained.

Properties of Oxygen gas.

1. Its action on test-paper.

Remove one of the cylindrical jars from the shelf of the trough, keeping its mouth under water; slide a ground glass plate over its mouth, and place the jar, thus covered, with its mouth upwards on the table. Take strips of blue litmus and reddened litmus-paper, and moisten them with distilled water; then remove the cover from the jar of gas, and dip the test-papers into the oxygen. You will observe, on withdrawing them, that the colour of neither test-paper is changed¹. Oxygen is therefore a 'neutral' substance.

2. Its relation to ordinary combustion.

Place another of the cylindrical jars of gas, its mouth upwards and closed with a glass plate, on the table before you, near the lighted lamp. Take in the right hand the piece of wax taper attached to a bent wire (fig. 12, p. 8) and light it at the lamp; then, withdrawing the glass plate, introduce the taper into the bottle of gas. Notice that it is not extinguished, but burns with a whiter, more intense flame.

Its action on a glowing splinter of wood, causing it to burst sharply into brilliant combustion, has been observed already, and need not be tried again.

3. Its affinity for other radicles.

Oxygen combines, more or less readily, with almost all other radicles; and the compounds formed are called 'Oxides.' Thus in the experiment last made, oxygen united with the carbon and hydrogen of the taper to form carbon dioxide and hydrogen oxide (water). The following are other examples of the 'burning' or 'combustion' of substances in oxygen; the phrase simply meaning the combination of the two radicles with production of great heat.

¹ If the evolution of gas has been rapid, chlorine and chlorine oxides may be present in sufficient quantity, to be recognised by their odour (pure oxygen being inodorous), and to redden and bleach the litmus-paper in a short time.

(a) Combination of oxygen with sulphur.

Place the large bottle of gas on the table before you. Take the deflagrating cup and adjust its position (holding it by the side of the bottle) by sliding the rod through the flange so that it may, when placed in the bottle, hang about 2 or 3 cm. from the bottom of the bottle. Place in it a piece of sulphur, about as large as a pea. Loosen the stopper of the bottle of gas with the left hand; hold the deflagrating cup for a few moments in the flame of the lamp (keeping the rod slanting so as to heat the cup only) until the sulphur melts and finally catches fire, and then immerse it in the bottle. The sulphur, which was burning in the air with a faint lambent blue flame, will immediately begin to burn much more¹ brilliantly, while white clouds are formed in the bottle¹. It is, in fact, combining with oxygen, giving out intense heat in doing so, and forming a substance called 'sulphur dioxide.' When the combustion is over, take out the cup, and observe the pungent suffocating smell of the sulphur dioxide which has been produced. Both oxygen (when pure) and sulphur are quite free from smell, as you will have noticed already.


Dip a piece of moistened blue litmus-paper into the bottle: observe that its colour is changed to red. Substances which change the colour of litmus from blue to red are said to have an 'acid reaction².' In this case the sulphur dioxide has combined with the water with which the paper was moistened, to form hydrogen sulphite, or 'sulphurous acid.'

¹ Sulphur dioxide is, as will be hereafter seen, a transparent colourless gas; the white fumes are due to its combination with the moisture in the bottle.

² The reason why the colour of the litmus is changed from blue to red by an 'acid,' and from red back again to blue by an 'alkali' (such as calcium hydrate, p. 67) is as follows. The true colouring matter of litmus is a substance of a red colour; this in ordinary blue litmus is combined with sodium or ammonium forming a blue salt. When a stronger acid is brought into contact with this, it combines with the sodium, or other radicle, liberating the red colouring matter. When an alkali, such as calcium hydrate, is added, it combines with the colouring matter, forming a salt which is blue.

(b) Combination of oxygen with iron.

Place the deflagrating jar, standing in a plate containing water, on the table before you. Take a piece of very thin watch-spring (readily obtained from any watchmaker), about 20 cm. in length, or more, and soften it by heating it to redness in the flame of a Bunsen's burner and allowing it to cool slowly. When it is cool it will be found to have lost much of its elasticity, and can be straightened without difficulty. Take the flange, or flat plate, of the deflagrating cup (the rod and cup being, of course, removed), and pass through it the piece of watch-spring so far that, when the flange is placed on the neck of the deflagrating jar, the end of the watch-spring may hang straight down to within 3 or 4 cm. of the plate in which the jar stands (try this by holding it at the side of the jar): a small wedge, such as the end of a match, will secure it in this position.

Bend up this end of the spring so as to form a small loop, thus  (actual size), in which fasten securely a bit of German tinder or (which will do quite as well) a bit of one of the common cigar-lights made of touch-paper, and sold in strips. Loosen the stopper of the deflagrating jar with the left hand, while with the right hand you take up the flange with watch-spring attached. Light the tinder at the lamp, and immediately take out the stopper, and steadily lower the watch-spring into the gas until the flange rests on the neck of the jar, in which position it should be held by the hand. The tinder will continue to burn, and the watch-spring, becoming red-hot, will also enter into brilliant combustion, sending out sparks and fusing into globules of iron oxide, which will fall off into the water in the tray. Be careful to take out the watch-spring as soon as the combustion comes near the neck of the jar, or the latter may be cracked by the heat.

The oxygen has here combined with the iron of which the watch-spring is chiefly composed, to form two oxides; one consisting of black, brittle globules which fall off the end of the spring into the water; and the other consisting of a brown

powder, adhering to the sides of the jar, which is nearly the same in composition as common iron rust¹.

(c) **Combination of the oxygen of air with magnesium.**

When substances burn in air, the action in all cases really consists in their combination with the oxygen of the air, forming oxides. For example, take a bit of magnesium ribbon about 8 or 10 cm. long, and, holding one end in the crucible tongs, bring the other end into the flame of a Bunsen's burner. The metal will take fire and burn with a brilliant bluish white light, as it combines with the oxygen of the air to form a white powder, which is magnesium oxide.

[Other examples of the direct combination of substances with oxygen are given under the heads of CARBON, PHOSPHORUS PENT-OXIDE, and COPPER.]

2. HYDROGEN.

[Symbol of atom,	H
Weight „	1 hydrogen-atom ² .
Formula of molecule,	H ₂
Weight „	2 hydrogen-atoms.]

Apparatus required.—Pneumatic trough; two gas jars, 20 × 5 cm.; one ditto, 10 × 3 cm.; flask, with flat bottom, holding about 250 c.c.; bent delivery tube, used in the last Exercise; thistle funnel; corks; cork-borers; rat-tail file; retort-stand; piece of wire-gauze; taper on wire; glass disc, 8 cm. in diameter; gas tray, 8 cm. in diameter; Bunsen's burner; Bunsen's holder; drying tube (fig. 48, p. 12); india-rubber tubing, for connectors; glass jet (p. 32); large beaker or funnel; glass tube about 30 or 40 cm. long and 1 or 1.5 cm. in internal diameter; jug of water; cloth.

Granulated zinc (see p. 26); strong (common) hydrogen sulphate; small tuft of asbestos; solution of platinum perchloride; distilled water; small bottle of oxygen gas (unless a supply can be obtained from a gas-holder); plaster of Paris.

¹ The beauty of the combustion is almost entirely due, not to the iron, but to the carbon present in the steel watch-spring; as may be shown by repeating the experiment, substituting for the spring a piece of pure iron wire ('binding wire') coiled into a spiral by being wound round a test-tube or glass rod about 1 cm. in diameter. In this case the metal will simply burn with a steady glow, emitting few or no sparks according to the purity of the iron.

² The hydrogen-atom, being the lightest of all known atoms, is taken as the unit, or standard, to which the weights of other atoms are referred.

Hydrogen is usually prepared by the action of the force of chemical affinity upon certain compounds containing it. An experiment has already been made (p. 80) which shows that, when zinc is caused to act upon hydrogen chloride, the latter is decomposed, the zinc combines with the chlorine, while hydrogen gas is liberated. If hydrogen sulphate (common sulphuric acid), diluted with water, is acted on by zinc or iron, a precisely similar action takes place; and this is the usual process for obtaining hydrogen.

[Other chemical actions in which hydrogen is formed are given under the head of NITRATES (action of zinc on potassium hydrate), and POTASSIUM (action of potassium on water).]

Preparation of Hydrogen gas.

Get ready the pneumatic trough as for the preceding exercise. Instead of bottles it is best to use plain cylindrical jars, ground at the mouth, about 5 cm. in diameter and 20 cm. high. Fill two of these with water and arrange them on the shelf of the trough. Now take the bent delivery tube, used in the preparation of oxygen; select a sound cork which will, after being squeezed, fit the neck of the flask; bore two holes in it (fig. 38, p. 38), one large enough to admit the delivery tube, the other adapted to the tube funnel. If none of your cork-borers will make holes of the precise size required, use the next smaller cork-borer, and enlarge the holes with the rat-tail file. Fit the short branch of the delivery tube into the cork until its end just appears on the opposite side; then with a screwing motion pass the tube of the funnel through the other hole in the cork until the lower extremity, when the cork is fitted into the neck of the flask, would reach nearly to the bottom.

Weigh out 30 grms. of granulated zinc, and place it in the flask, sliding the pieces down the neck, held slanting (not dropping them in, lest they should break the flask); support the flask in the retort-stand on wire-gauze¹, and fit the cork firmly into its

¹ Although the flask does not, in the present case, require to be heated, yet it is advisable to place under it a piece of wire-gauze which serves as an elastic cushion.

place. The flask should be supported at such a height that the end of the delivery tube may be just below the hole in the shelf, and not unnecessarily deep in the water. Fig. 72 shows the apparatus thus arranged.

Pour through the funnel enough distilled water to cover the zinc to the depth of 1 cm., and try whether the joints are tight

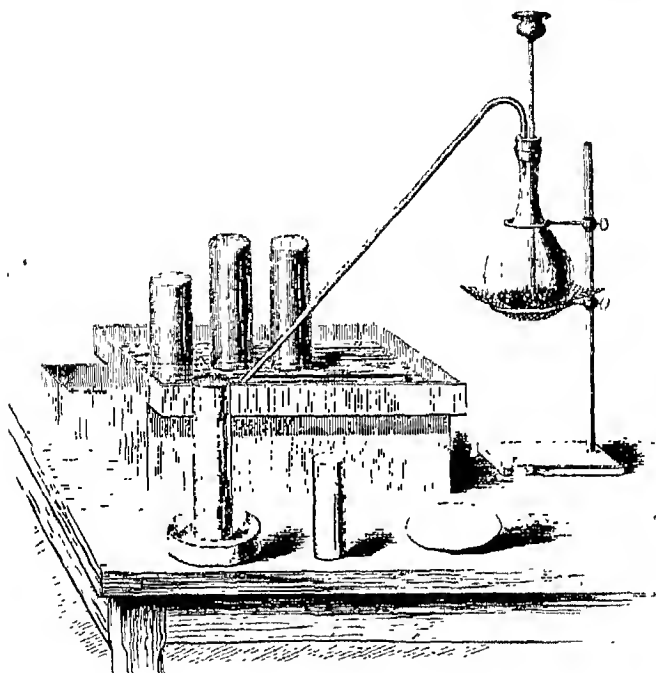


Fig. 72.

by placing the warm hands on the flask for a few seconds. This will expand the air within, which will raise a column of water in the funnel tube (depressing, of course, the water in the delivery tube to an equal extent). If on withdrawing the hands this column remains steady for a moment, and only sinks gradually to its former level, the joints may be considered good. If, however, the column either does not rise at all, or sinks rapidly when the warmth is withdrawn, there is a leak

somewhere in the cork-joint. This may often be remedied by wetting the cork and the tubes with water before fitting them into their places, and pressing the cork more firmly into the neck of the flask: otherwise it will be best to take a new cork. Do not proceed with the preparation of the gas until the joints are all quite air-tight, since hydrogen escapes through small cracks far more quickly than any other gas.

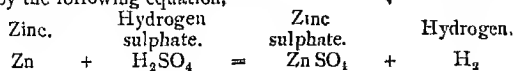
Pour about 2 c.c. (about a tea-spoonful) of strong common (not the pure acid used in Analysis) hydrogen sulphate down the funnel, and shake the flask, so that the acid and water may mix. When this reaches the zinc an effervescence will commence, owing to the liberation of hydrogen. After about half a minute a little more acid may be poured through the funnel, so as to keep up a rapid stream of bubbles from the delivery tube; but especial care should be taken not to add too much at a time, lest the action should become too violent, partly from the undue strength of the acid, partly owing to the heat evolved from the mixture of the acid with the water. If the liquid in the flask should show a tendency to froth over, pour some water down the funnel, to dilute and cool the acid. It is often the case that the action is slow at first, but it is better to give it a little time than to add acid recklessly¹.

- [The action may be expressed as follows² :—

Substances taken.	Composition	Substances obtained.
Zinc, 65 parts.	-----	Hydrogen, 2 parts.
Hydrogen sulphate, 98 parts.	{ Hydrogen, 2 parts (Sulphur, 32 parts) { Oxygen, 64 parts	{ Zinc sulphate, 161 parts.

¹ Pure zinc and some varieties of granulated zinc do not always act readily on the acid. If, after all, only a slight effervescence occurs, pour into the funnel one or two drops of solution of platinum perchloride and wash it into the flask with a little water. This will, owing to the galvanic action between the reduced platinum and the zinc, greatly increase the rapidity of the evolution of the gas.

² Or by the following equation,—



Fill three of the larger jars with the mixture of air and hydrogen which first escapes from the flask, and reject their contents before proceeding to collect the gas for your experiments. This precaution is of more importance here than in the case of oxygen, because (as will appear) air forms with hydrogen a mixture which explodes upon contact with a light, and you may have an awkward, if not dangerous, mishap, if you unintentionally experiment with such a mixture instead of pure hydrogen. After sacrificing this quantity, however, you may safely collect two of the larger jars full of the gas, precisely as directed in Exercise 1, sliding the jars over the hole in the shelf, and when each is full removing it to the side shelf of the trough. It is best not to fill the jar completely with gas (as it may topple over), but only so far that the water in the tray and in the jar may stand at the same level. It should, of course, be filled up completely with gas before being used for experiments. While the jars are being filled with gas, you may calculate the quantity of hydrogen obtainable by the action of the 30 grms. of zinc upon excess of hydrogen sulphate¹. Add from time to time a little more strong hydrogen sulphate, to keep up the stream of gas, but manage so that the action may be subsiding while the last jar is being filled, so as to avoid unnecessary waste of gas. When the jars are full, leave the flask and delivery tube in their position for the present, and examine the following properties of the gas.

Properties of Hydrogen gas.

1. Its freedom from colour and smell will have been noticed already.
2. Its insolubility in water is sufficiently proved by the fact that it can be collected over water in the pneumatic trough.
3. Its action on test-paper.

This may be sufficiently tested by holding strips of blue

¹ The calculation should be made on the same principles as already explained in the case of oxygen (see p. 120, note). The question is,—If 65 parts by weight of zinc cause the liberation of 2 grms. of hydrogen, how much will be obtained by the use of 30 grms. of zinc? (1 litre of hydrogen weighs 0.09 gm. nearly.)

and red litmus-paper over the bubbles as they rise from the delivery tube. The gas will be found to be neutral, like oxygen.

*4. Its relation to ordinary combustion.

Transfer one of the jars of gas, mouth downwards (using a gas tray), from the trough to the table. Take the taper attached to the bent wire (fig. 11, p. 8) and light it: then with the other hand raise the jar of gas steadily from the water, keeping its mouth still downwards, and immediately pass the lighted taper up into it. The gas will take fire with a slight noise where it is in contact with the air, and burn with a pale, almost invisible flame; but the taper on being pushed further into the gas will be extinguished. Now withdraw the taper quickly and turn the mouth of the jar upwards; the flame will pass rapidly down the jar, and the gas will be found to have disappeared entirely.

[The jar may now be refilled with gas, for use in other experiments.]

5. Its lightness as compared with common air.

This will be sufficiently proved if it is found capable of being poured upwards through air; just as a cork is proved to have a smaller density than water (for an explanation of 'density' see p. 50) because it rises through water.

Transfer another of the larger jars of gas from the trough to the table. Take a small gas jar (empty) and hold it inverted in one hand, as shown in fig. 73 (next page). Raise the jar of gas out of its tray with the other hand, bring its mouth near the edge of the small empty jar, as shown in the figure, and steadily depress the closed end, proceeding exactly as if you were pouring a liquid upwards from it into the smaller jar. Set down the small jar, which is in your left hand (mouth downwards), in the tray of water; light the taper affixed to the wire and bring it into the up-turned mouth of the other jar. The gas will be found to have escaped entirely, the taper burning as in the outer air. Now raise the mouth of the small jar above the level of the water in the tray, and pass up into it the lighted taper. A

slight explosion will take place, as the gas catches fire, thus demonstrating that the hydrogen has really ascended and displaced the air in the jar, precisely as it displaces the water in filling a jar at the pneumatic trough.

6. Its combination with oxygen, to form water.

When water is decomposed by an electric current or otherwise, the volume of hydrogen obtained is twice that of the oxygen. We may therefore infer that the gases must be mixed

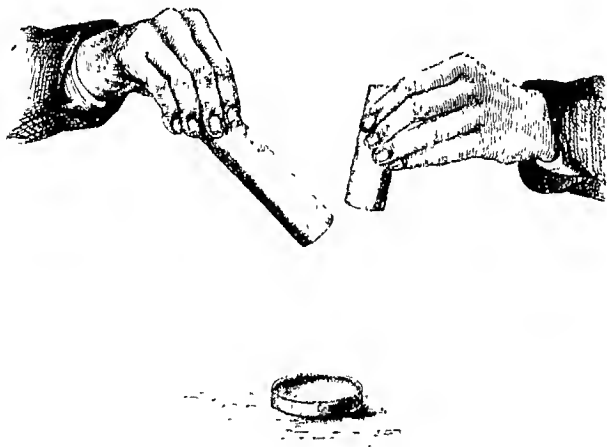


Fig. 73.

in the proportion of two measures of hydrogen to one measure of oxygen, in the formation of water by synthesis.

Fill with water both the jars used in the last experiment, and place them on the shelf of the pneumatic trough. Fill the smaller jar (which is to serve as the measure of volume) with hydrogen from one of the remaining jars of gas, and decant its contents into the larger jar. Fill it again with gas, and again decant its contents, as before. You have now two measures of hydrogen in the larger jar. Next fill the small jar with oxygen from one of the bottles reserved in the last Exercise (or from a gas-holder), and decant this measure of oxygen into the jar containing the two measures of hydrogen.

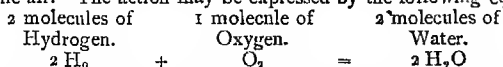
Depress the jar in the trough, and shake it sideways to mix the gases (taking care that no air enters); then fill the small jar with the mixed gases, close its mouth with a glass plate, remove it from the trough and place it on the table, mouth upwards, retaining the glass plate in its position with the left hand. Light a match, withdraw the glass plate, and apply the lighted match to the mouth of the jar. The gases, hitherto only mixed, when thus heated combine suddenly with an explosion which, though loud, is quite unattended with danger if a small strong jar is used as above directed¹.

[Do not, on any account, apply a light to the mixed gases in the larger and thinner jar, since you may have a serious accident if the jar should break.]

[You may, if time allows, try two or three similar experiments, varying the proportions of hydrogen and oxygen (taking, for instance, two measures of oxygen and one of hydrogen), and you will find that the explosion, which accompanies the chemical combination, is loudest when one measure of oxygen is mixed with two of hydrogen, as in the original experiment. Hence we infer that when the gases are mixed in this latter proportion, the greatest possible amount of chemical combination takes place. This is found to be the fact when the combination is effected in a strong closed vessel: the whole of the gases then disappear, but if hydrogen and oxygen are mixed in any other proportion a quantity of one or the other remains uncombined.]

You may, further, try a few similar experiments, using air instead of oxygen. You have noticed, in Experiment 4, that when a lighted taper is passed into a jar of hydrogen the gas takes fire at the mouth of the jar, where it is in contact with the air. This is due to its combination with the oxygen, which is one of the constituents of air. Now, you will find that when air and hydrogen are mixed in the proportions of five measures of air to two measures of hydrogen², and a lighted match applied to the mixture (this may be

¹ The cause of the explosion is the sudden intense heat which is produced by the chemical combination: this produces a quick and enormous expansion in the steam which is formed, and thus there arises a violent sound-wave in the air. The action may be expressed by the following equation—



² If you have no jar large enough to contain seven measures of the gases,

done in the larger jar), an explosion takes place, much less violent than in the case of oxygen and hydrogen, but loudest when the above proportions of the gases are taken. But we have just seen that *two* measures of hydrogen unite with *one* measure of oxygen to form water. Hence five measures of air contain one measure of oxygen¹.]

7. Proof that water is the product of the union of oxygen with hydrogen.

This will be best observed by causing the combination to take place more slowly; for instance, by allowing a jet of hydrogen to burn in air.



Fig. 74.

Raise the delivery tube out of the water, and support the end of it upon a wooden block placed on the table (the flask being still retained in the retort-stand). Attach to it one of the elbow-tubes which you have already made, stretching over the ends of both a short piece of india-rubber tubing, slightly moistened to make it slip over the glass more easily. To the

put an india-rubber ring round the small jar about 2 cm. from its mouth, and reckon the contents of the jar to this level as one measure.

¹ The composition of air will be further illustrated in the next Exercise.

other branch of the elbow-tube, which should point vertically upwards (fig. 74), adapt in a similar way the glass jet you have already made (p. 32). Pour a little more acid on the zinc, if the stream of gas has ceased; and since air may have entered the flask, it will be advisable to test the purity of the gas before lighting it at the jet, in order to avoid the chance of an explosion. To do this, hold over the jet a small inverted test-tube, bringing the jet nearly to the closed end of the tube. We have seen that hydrogen can be poured upwards, therefore the tube will soon fill with gas. After about ten seconds raise the tube slowly from the jet, close its mouth immediately with the thumb, remove it to some distance from the jet, and, still holding the mouth downwards, apply a lighted match to it. If the gas burns quickly, with a shrill noise, air is mixed with it; and it will not be safe to light it at the jet. Other trials should be made, and when the gas catches fire with only a slight noise, the flame passing slowly along the tube, it is pure and you may proceed with the experiments.

Pour a little more acid on the zinc in the flask, if necessary, and light the hydrogen issuing from the jet. When it burns steadily with a flame about 2 cm. high¹, hold over it a clean dry beaker or bottle (inverted), so that the flame may be just level with its mouth, and notice that a dew is at once deposited on the glass, soon collecting into drops of a colourless liquid, which is pure water. It will be hardly worth your while to collect much of the liquid, but you may at any rate satisfy yourself that the product of the combustion is tasteless, and that when the outside of the glass is gently warmed by moving it to and fro over the lighted jet of gas the deposit volatilises without leaving any residue. Tastelessness and ready volatility are two of the properties of water.

8. Musical note produced by the hydrogen flame.

When the current of gas has slackened, but is still burning at the jet, another experiment may be tried which shows in

¹ The flame will shortly become yellow, owing to a trace of sodium, contained in the glass of the jet, becoming volatilised.

an interesting way that the flame, under certain conditions, although apparently steady, is really expanding and contracting; is, in fact, rather a series of flames quickly succeeding one another, than a continuous flame.

Hold a glass tube, about 30 cm. in length and about 1.5 cm. in diameter, over the jet, and depress it gently until the flame is entirely within the tube. At a certain point the flame will become elongated and a musical note will be produced varying in pitch with the length of the tube, and also, for the same tube, with the size of the flame. This sound is due to the fact that the air in the tube is set in vibration by the extremely rapid succession of explosions caused by the combination of the hydrogen, as it issues from the jet, with the oxygen of the surrounding air.

The fact is, that hydrogen and oxygen only combine when mixed in a certain proportion. This mixture takes time to form, but as soon as it is formed the combination is sudden. A distinct interval then occurs before the due mixture is again formed; this is exploded by the heat of the previous combination; another pause occurs; then another explosion, and so on. These explosions follow each other so rapidly as to convey to the ear an impression (not of a series of noises, but) of a clear continuous musical note.

9. Readiness with which hydrogen diffuses.

Put out the flame, and hold a piece of blotting-paper close above the jet from which the gas is still issuing. Bring a lighted match near the upper side of the blotting-paper, just over the jet. The gas will catch fire, showing that it has passed quickly through the pores of the paper, as through a sieve.

Additional Experiments.

10. Action of platinum in causing the combination of oxygen and hydrogen.

This will be more fully explained hereafter (see under PLATINUM), but it may be tried in a simple way thus,—Take a small tuft of asbestos, and coil the end of a piece of platinum wire once or twice round it to serve as a handle: then moisten it with a drop of solution

of platinum perchloride placed in a watch-glass, and hold it, first above and then in the flame of a Bunsen's burner, until the salt is decomposed and a gray deposit of finely divided platinum is left on the asbestos. Allow this to cool, and then hold it just above the jet, in the stream of gas. It will become red hot, showing that it is causing the combination of hydrogen with the oxygen of the air, and the gas will shortly catch fire.

11. Strict proof that water is formed when hydrogen and oxygen combine.

It must be observed that we have not yet rigorously proved that water is formed during the burning of hydrogen in air, since no pains have been taken to dry the gas, which of course contains moisture derived from the liquid in the flask. In order that the experiment may be decisive, the hydrogen must be passed over some drying material before it is burnt at the jet.

Take off the glass jet and india-rubber connector, and fit the end of the elbow-tube into the cork at the end of a drying tube (fig. 23, p. 12) filled with fragments of quicklime or of calcium chloride. Support the drying tube in a vertical position by the Bunsen's holder, and fit the jet upon its upper end. Test the purity of the gas, as already directed, p. 133. When you are sure that it is unmixed with air, light it at the jet, and hold a beaker over it, as in experiment 7. If moisture is now deposited on the beaker, water must have been formed during the combustion, since the gas has been dried, and the air contains too little moisture to form any deposit on the glass.

12. Lightness of hydrogen.

Make a solution of soap by dissolving in a small evaporating dish a bit of common soap as large as a pea in 5 or 6 c.c. of water. Remove the glass jet, and touch the end of the india-rubber tube with a finger dipped in the soap solution. A bubble will soon be blown, which when it leaves the tube will ascend rapidly. One or two trials with soap solution of various strengths and more or less warm may be required to get a good result¹.

¹ A solution which keeps well and forms good bubbles may be made as follows.

Dissolve 5 grms. of pure sodium oleate (made by gently heating 5 grms. of sodium hydrate with 25 grms. of oleic acid) in 80 c.c. of distilled water. When cold add 5 c.c. of glycerine and mix thoroughly. The solution should be shaken up before use, and the clear portion poured off into a porcelain dish.

[If you possess one of the small fish-skin balloons sold by opticians, the lightness of hydrogen gas may be further demonstrated in the following way:—

In the first place ascertain that there are no holes in the balloon by expanding it with air and holding it between your eye and the light, turning it round to examine every part of it¹. If any holes are visible, they may be mended by touching the margins with weak gum-water and covering them with small patches of gold-beater's skin. A short piece of quill should be inserted in the neck of the balloon, and secured in its place by folds of thread. Take off the glass jet from the apparatus used in the preceding experiment, and, having carefully squeezed and sucked out as much as possible of the air from the balloon, stretch the india-rubber connector over its neck, and proceed to fill it with gas, pouring a little more acid on the zinc whenever the current of gas becomes slow. When the balloon is full, you may allow it to ascend in the room, after inserting a small plug of cork into the neck, and attaching a long piece of thread to the quill, in order to have the movements of the balloon under control.]

13. Diffusion of hydrogen through plaster of Paris.

Take a piece of glass tube about 25 cm. long, and 1 cm. internal diameter (a piece of 'combustion tube,' or the tube used in expt. 8, will do) and fit a cork to one end. Pour about 10 c.c. of water into a small porcelain dish, and add enough plaster of Paris to form a thin paste, stirring it thoroughly with a glass rod. Before it sets, plunge into it one end of the glass tube (the cork being withdrawn) until it rests on the bottom of the dish, and support it upright in a Bunsen's holder until the plaster has got moderately hard, which it should do in four or five minutes. Then carefully detach it from the surrounding plaster, and push the cork a little way into the tube so as to drive the plug of plaster before it. Take out the cork, and dry the plaster thoroughly by a gentle heat; leaving it for several hours in a drying cupboard, or before a fire. When it is quite dry, insert the cork and fill it with hydrogen by placing it over the end of the jet, in the same manner as the test-tube was filled, p. 133, supporting it in a Bunsen's holder. While it is filling, pour some water into a large beaker and add a drop or two of indigo sulphate to colour it. In about a minute, if there is a fair stream of gas, the

¹ These balloons are very liable to be attacked by insects. They should be kept in a wide-mouthed bottle or tin jar with a small bit of camphor.

tube will be sufficiently full. Its lower end should now be immediately dipped into the water in the beaker and the cork withdrawn from the upper end. The hydrogen will diffuse out through the plaster plug so much faster than the air diffuses inwards that the water will rise in the tube and partly fill it.

[After trying the above experiments, you may take the apparatus to pieces, wash the tubes, and set them aside to dry. The liquid which is in the flask is a solution of zinc sulphate, and may be filtered into an evaporating dish, and evaporated as directed in Sect. I, Ex. 5 (p. 62), until it deposits crystals on cooling. The zinc sulphate thus obtained is very pure, and may be reserved for use in the laboratory.]

3. NITROGEN.

[Symbol of nitrogen-atom,	N
Weight	14 hydrogen-atoms
Symbol of nitrogen-molecule, N_2	
Weight	28 hydrogen-atoms.]

Apparatus required—Pneumatic trough; porcelain dish 6 cm. in diameter; gas tray; deflagrating jar; two gas jars, 20×5 cm.; one gas jar, 10×3 cm.; small gas bottle; beaker about 6 cm. in diameter; glass disc; taper on wire; jug of water; cloth; blotting-paper; crucible tongs; knife; test-tubes.

Phosphorus; tow; turpentine; test-papers.

Nitrogen is usually obtained from common air. It was formerly thought that air was an element, but very simple experiments suffice to show that it consists of at least two substances differing from it and from each other in properties. To prove this,—

Fill the pneumatic trough with water, and place on the shelf one of the larger cylindrical jars, mouth downwards, and full of air. Light the taper affixed to the wire (fig. 11, p. 8), raise the mouth of the jar slightly above the water, and pass up into it the taper, immediately lowering the mouth of the jar again beneath the surface of the water, so that the candle may burn in a definite volume of air enclosed in the jar. The flame will very shortly grow dim, and finally go out, and the water will rise to a certain height in the jar, but not very far. Since it is known that no substance insoluble in water is formed when a candle burns in air, you have thus proved that air consists of at

least two gases:—one which supports the combustion of a candle, and which can be proved to be oxygen,—and another in which a candle will not burn, and which forms by far the largest proportion of air. This latter gas is nitrogen.

Preparation of Nitrogen.

The principle of the usual method of obtaining the gas is indicated in the experiment just made; *viz.*, to withdraw from air all the oxygen it contains by the action of some substance which has an affinity for oxygen but not for nitrogen. Phosphorus is, on the whole, the best substance for the purpose, since it readily combines with oxygen and the compound formed (phosphorus pentoxide) is very soluble in water, and is therefore quickly withdrawn when the experiment is made over the pneumatic trough, leaving the nitrogen nearly pure.

[Read the precautions to be taken in dealing with phosphorus, given on p. 81.]

Float a small porcelain dish on the water in the pneumatic trough, retaining it over the movable shelf. Take a stick of phosphorus from the bottle with the crucible tongs, place it in a gas tray full of water, and cut off with a knife (still holding it under water) a piece about twice as large as a pea. Dry the piece of phosphorus thoroughly, by *gently* pressing, not rubbing, it between folds of blotting-paper; then place it at once, using the (dried) crucible tongs, in the floating dish. Take the stopper (which should be greased) out of the deflagrating jar, and, holding the jar in one hand over the phosphorus, light the latter by touching it with a burning match; then lower the jar at once over the burning phosphorus until it rests upon the shelf of the trough, and immediately insert the stopper. The level of the water in the jar will at first be depressed, owing to the expansion of the enclosed air by the heat of combustion, but it will soon rise above the level of the water in the trough, showing that one of the constituents of the air is being withdrawn. When the phosphorus ceases to burn, allow the jar to remain undisturbed for five minutes, until the white fumes (which consist of a compound of phosphorus with oxygen, phosphorus pentoxide) have

been for the most part absorbed, and meanwhile fill all the gas jars with water and place them inverted on the shelf of the trough. Fill also the large beaker, which is to be used precisely as a gas jar, its large, spreading mouth rendering it easier to avoid loss in decanting gas into it from the deflagrating jar.

When the white fumes have nearly cleared away, depress the deflagrating jar in the trough and shake it laterally until the small dish is filled with water and sinks to the bottom, when it may be withdrawn. Decant some of the nitrogen first into the beaker (remembering not to fill it completely, lest it should topple over) and then from the beaker into the three gas jars.

Properties of Nitrogen.

1. Its action on test-paper.

Raise the mouth of the smallest gas jar above the water of the trough (still keeping it inverted, since nitrogen is rather lighter than air), and pass up into it strips of moistened blue and red litmus-paper. The gas will be found to be neutral, like hydrogen and oxygen.

2. Its relation to ordinary combustion.

(a) Slide one of the larger jars of gas off the shelf of the trough, cover its mouth with a glass plate, lift the jar out of the water, retaining the plate in its position with one hand, and place it on the table mouth upwards¹. Light the piece of taper affixed to the wire (fig. 12), remove the glass plate from the mouth of the jar, and plunge the lighted taper into the gas, withdrawing it again as soon as the result has been observed. Notice that the taper is extinguished while the gas itself does not catch fire; thus showing it to differ from oxygen, in which the taper continued to burn, and from hydrogen, which extinguished the taper, but was itself inflamed.

[If the glass plate is at once replaced on the jar, the same jar of gas may be used for the next experiment.]

(b) Remove the taper from the wire, and in place of it twist a

¹ This position is most convenient, although the nitrogen will escape rather more quickly than from an inverted jar.

small piece of tow round the end of the wire, so as to form a ball about 1 cm. in diameter. Pour a few drops of turpentine on the ball of tow, set it on fire, and immerse it in a jar of nitrogen. The flame will be as instantly and completely extinguished as the small flame of the taper in the last experiment.

These are all the experiments which can be readily tried with nitrogen, which in the free state appears as an inactive gas, showing very slight chemical affinities.

[Reserve a jar or small gas bottle full of nitrogen for use in the next series of experiments.]

4. AIR.

Apparatus required—Pneumatic trough; gas jar, 20 × 5 cm.; small gas jar, 10 × 3 cm.; small gas bottle; graduated measure holding 200 c.c.; porcelain mortar; test-tubes; beakers; watch-glass; corks; cork-borers; elbow-tubes, one with long branch; taper on wire; india-rubber rings about 2.5 cm. in diameter; piece of small-sized india rubber tubing, about 40 or 50 cm. long; piece of fine brass wire 30 cm. long.

Phosphorus; dry calcium chloride; solution of calcium hydrate (lime water); ether; bottle of nitrogen (reserved from the last exercise); small bottle of oxygen (unless a supply can be obtained from a gas-holder).

Composition of Air.

You have already made an experiment (p. 137) which proves that air consists of more than one substance, and you have separated and examined one of its ingredients, nitrogen. The other chief ingredient, oxygen, cannot, unfortunately, be obtained from it in the free condition by any simple means. You may now proceed to examine more exactly in what proportions these two ingredients, nitrogen and oxygen, are present in ordinary air.

We may obtain proofs of the exact composition of air in two ways:—

(a) By analysis; *i. e.* by separating it into substances which we can prove to be oxygen and nitrogen, and observing the quantities of each, which are obtained from a given amount of air.

(b) By synthesis; *i. e.* by mixing oxygen and nitrogen in the

proportions indicated by analysis, and observing whether the resulting product has the same properties as air.

Analysis of Air.

For this purpose we may conveniently employ phosphorus: not, however, kindling it and thus causing it to withdraw the oxygen quickly, but allowing it to act at the ordinary temperature for several hours. The cylindrical measure will do pretty well instead of a regular gas measuring-tube, if one of the latter is not at hand.

Fill a small test-tube about half-full of water, put into it enough phosphorus to form a stratum about 1 cm. deep, and place the tube in a beaker of nearly boiling water until the phosphorus is melted. Make a small loop at the end of a piece of fine brass wire about 30 cm. long, by coiling it round a glass rod or pencil, plunge the looped end of the wire into the liquid phosphorus, and cool the tube by holding it in cold water. When it is quite cold, fill up the tube with water, pull out the wire with the lump of phosphorus attached to it (this may require the tube to be dipped into hot water again for a moment only, to loosen the phosphorus from the sides), and put it at once into a dish of water until wanted.

Put the graduated cylindrical measure mouth downwards into a porcelain mortar nearly full of water, pushing up into it the end of a piece of small india-rubber tube. Suck air out of the jar through the tube until the water level inside stands exactly at the mark 200 c.c.; then pinch the tube to prevent air entering or escaping, and withdraw it from the jar. Incline the jar a little and introduce the lump of phosphorus, pushing it up by means of the wire nearly to the closed end of the jar. Restore the jar to its vertical position and leave it undisturbed in a safe place for 12 or 14 hours¹.

[Meanwhile the other experiments on air may be proceeded with.]

At the end of this time, pull out the phosphorus attached to

¹ It should not be left for more than a day, otherwise the air which diffuses through the water will vitiate the results.

the wire (placing it at once under water¹), and read the volume of the remaining gas. To do this it will be best to transfer the jar to the pneumatic trough, and lower it in the water until the level inside and outside the tube is the same. You will find that out of the original 200 c.c. of air, only 160 c.c. (approximately) remain; and this residual gas may be shown to be nitrogen by decanting some into a gas jar and testing it with a lighted taper. And since the white fumes formed during the action of the phosphorus are known to consist solely of a compound of phosphorus and oxygen, the $(200 - 160 =) 40$ c.c. of gas which have disappeared, may be assumed to be oxygen.

Then the percentage composition of air by volume can be found by the proportion sum

200 : 40 :: 100 : percentage of oxygen,

and $100 - \text{the percentage of oxygen} = \text{the volume of nitrogen and other gases in 100 parts of air.}$

Notice the peculiar oppressive smell of the gas remaining in the jar: both oxygen and nitrogen being quite odourless. This is due to the presence of a peculiar modification of oxygen called '*ozone*,' formed during the slow oxidation of the phosphorus.

2. Synthesis of Air.

Take one of the larger cylindrical gas jars, and graduate it into five parts in the following way. Try first whether the large jar will hold not less than six of the small jars full of water. If it holds less than this, slip an india-rubber ring over the small jar, about 1 cm. from the mouth, fill the jar with water up to the level of the ring, and try whether about six times this reduced volume will fill the larger jar. One or two trials will be sufficient to ascertain the proper volume, which is to be the unit of measurement. Now fill the measure (*i.e.* the small jar) up

¹ To detach the phosphorus from the wire, put it into a test-tube containing a little water and immerse the end of the tube in hot water until the phosphorus has melted, when the wire may be withdrawn. The test-tube should be left in a slanting position until the phosphorus has solidified; the latter may then be shaken out and returned to the bottle.

to the proper point with water, pour the water carefully into the larger jar, and mark the level at which it stands by a small india-rubber ring slipped over the jar. Add another measure of water, and mark the level similarly with another ring. Proceed thus until five measures of water have been poured into the larger jar. You have now a jar graduated with sufficient accuracy, which should be filled with water and placed inverted on the shelf of the pneumatic trough. Decant into it sufficient nitrogen, from the bottle which was reserved, to fill it to the level of the fourth division: then add one measure of oxygen (from one of the bottles reserved in Ex. 1, or a gas-holder), cover the mouth of the jar with a glass plate, and invert it once or twice (retaining the glass plate firmly in its place with one hand) so as to mix the gases thoroughly. Observe that no heat is produced, as would be the case if the gases were chemically combining. Place the jar mouth upwards on the table and immerse in it a lighted taper. The latter will not burn brilliantly as in oxygen (p. 121) or be extinguished as in nitrogen, but will continue to burn as it did in the external air¹. Other experiments would show that the mixture possessed all the properties of common air, and thus we have a proof by synthesis that 5 volumes of air consist (approximately) of 4 volumes of nitrogen and 1 of oxygen.

3. Experiments upon other substances present in air.

Besides oxygen and nitrogen, perceptible quantities of carbon dioxide and water vapour are present in air. Their presence may be shown as follows:—

(a) Carbon dioxide.

Pour a little lime water into a watch-glass, and leave it exposed to the air for ten minutes or more. A white film will form on the surface, proving the presence of carbon dioxide in the air of the room.

¹ The brilliancy may be slightly increased, since air is not *entirely* freed from oxygen by the action of phosphorus under the above conditions, and hence the mixture would contain rather more than the proper amount of oxygen.

(b) **Water vapour.**

Pour a few drops of ether¹ into a large dry test-tube (taking care that no lighted lamp is near) and make it evaporate quickly by blowing air into it through an elbow-tube (best with a pair of bellows, since the warmth of the breath interferes with the cooling effect). The outside of the tube will become very cold, and cool the air near it; and a deposit of dew or even ice will appear on it, proving that water vapour is present in air, and only requires to be cooled down to a certain point in order to be condensed and show itself in a visible form.

Both the carbon dioxide and the water vapour in air come chiefly from very similar sources, *viz.* the combustion of candles, fires, &c., and the breathing of animals. These facts may be illustrated in the following way.

Sources of the carbon dioxide.

1. The burning of candles.

Put a little lime water into a small gas bottle, and shake it up. It will not become cloudy, since the amount of carbon dioxide in the air contained in the bottle is extremely small. Now light the taper affixed to a wire, place it in the bottle, and allow it to burn there, laying the stopper loosely on the mouth of the bottle, to prevent entrance of air. When it goes out, remove it from the bottle, insert the stopper and shake up the lime water. It will become milky, proving that carbon dioxide has been formed; the carbon of the wax having combined with the oxygen of the air.

2. The breathing of animals,

An experiment showing that carbon dioxide is produced in respiration has already been made, p. 69: it may be repeated in a more exact way, as follows.

Adapt a cork to a large test-tube (taking care to soften the

¹ If ether is not at hand, benzoline (such as is used for lamps) will answer; or a little pounded ice (or snow) and salt may be put into the tube. Or a freezing mixture may be made by mixing 8 grms. of finely powdered sodium sulphate with 5 c.c. of strong common hydrogen chloride.

cork thoroughly by squeezing it, or it may break the tube); bore two holes in the cork and fit into them elbow-tubes as shown in fig. 75. The long branch of one elbow-tube should reach nearly to the bottom of the test-tube, the short branch of the other should only just pass through the cork. Fill the test-tube about one-third full of lime water, and suck air through the liquid for a few seconds, applying the mouth to the extremity of the short elbow-tube. No turbidity will be produced, the quantity of carbon dioxide in the air being very small. Now, having taken a deep breath, apply your mouth to the other elbow-tube (the long branch of which passes into the liquid), and blow air from the lungs through the lime water. The latter will almost immediately become turbid, showing that much carbon dioxide is present in air which is expired from the lungs¹.

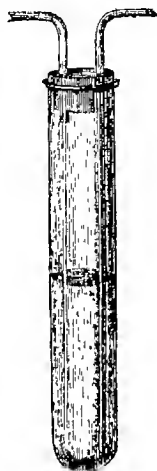


Fig. 75.

Sources of the water vapour.

1. The burning of candles.

Hold a beaker inverted over the flame of a gas burner or candle; its surface will become covered with moisture, owing to the combination of the hydrogen of the gas or wax with the oxygen of the air.

2. The breathing of animals.

Strew a little powdered calcium chloride upon a glass plate and breathe upon it. It will soon become liquid, showing that abundance of moisture is present in the breath.

¹ The reason why carbon dioxide does not accumulate in the air will be alluded to under the head of CARBON DIOXIDE (p. 194).

COMPOUND OF NITROGEN WITH HYDROGEN.

5. AMMONIA.

[Formula of molecule, H_3N

Weight „ 17 hydrogen-atoms.]

Apparatus required.—Florence flask; corks; cork-borers; elbow-tubes, one with long branch; drying tube, fig. 23; india rubber connector; retort-stand; Bunsen's holder; wooden blocks; sand-bath; argand burner; porcelain mortar; scales and weights; small porcelain dish; test-tubes; taper on wire; gas jar, 20×5 cm.; one large and four small gns bottles; glass disc; pan of water; beaker; flask with flat bottom, holding about 250 c.c.; piece of platinum wire about 15 cm. long; card; glass rod.

Ammonium chloride (sal ammoniac); quicklime; small bits of flannel (or silk) and calico; box of test-papers; strong solution of ammonia (ammonium hydrate); strong hydrogen chloride; dilute hydrogen sulphate; solution of indigo sulphate.

Sources of Ammonia.

Nitrogen and hydrogen can only with great difficulty be caused to unite directly; but when organic substances which contain both the elements, such as leather; wool, silk, or gelatine, are decomposed, some of the nitrogen and hydrogen unite to form ammonia. The following experiment illustrates this:—

Place a small bit of flannel (or silk) about 1 cm. square in a small test-tube, support it in a Bunsen's holder, as in fig. 62, p. 77, but nearly horizontally, and heat it rather strongly. The substance will become blackened or 'charred,' showing the presence of carbon: water will condense in the tube, proving that it contains hydrogen and oxygen; while strong-smelling volatile compounds of nitrogen will be given off, among which are ammonium carbonate and ammonia. The latter may be recognised (1) by its alkaline reaction on a strip of reddened litmus-paper moistened and held in the tube: (2) by the white fumes (of ammonium chloride) formed when a glass rod dipped in strong hydrogen chloride is held in the issuing vapours.

If a piece of paper or calico (substances which contain no

nitrogen) is heated in the same way, the vapours evolved will give no alkaline reaction or white fumes when tested as above¹.

Coal contains nitrogen, as well as hydrogen, oxygen, and carbon, and the compounds of ammonia obtained from it in the manufacture of coal-gas are acted on with hydrogen chloride (as illustrated in the second of the above tests) and form ammonium chloride ('sal ammoniac'). This salt is the usual source from which ammonia is prepared, as described below.

Preparation of Ammonia.

The gas is usually obtained by gently heating a mixture of ammonium chloride and quicklime. The precise nature of the action will be explained later (p. 149); but meanwhile it should be noticed that water is one of the products, and that the ammonia must be freed from water vapour by passing it over fragments of quicklime in a 'drying tube.' The gas is extremely soluble in water, so that it cannot be collected over the pneumatic trough (unless mercury instead of water is used). But it is so much lighter than air that it may be readily collected by upward displacement (p. 108).

Weigh out 15 grms. of sal ammoniac, and reduce it to powder in the mortar. The salt in its sublimed state is so tough as to render this rather difficult², and more may be effected by direct blows of the pestle, especially if aided by a thrust and slight twist of the arm at the moment of impact, than by the usual rubbing motion. Place the powdered salt in a basin and set it to dry on the sand-bath over the lamp, occasionally stirring it to prevent its caking together. Meanwhile reduce 30 grms. of quicklime to fine powder in the mortar³: then cover the mortar with a plate, to protect the lime from the moisture and carbon dioxide of the air.

¹ On the contrary, the vapours will be found to be acid, owing to hydrogen acetate (acetic acid) being formed.

² It should be bought in a state of powder if possible.

³ If the quicklime is very hard and difficult to powder, it may be slaked as directed on p. 66, care being taken to use as little water as possible, so that the calcium hydrate may be perfectly dry.

An apparatus should now be fitted up as shown in fig. 76.

Adapt a cork to a clean dry Florence flask, and fit into the cork an elbow-tube each branch of which is about 8 cm. long. Fill the drying tube with fragments of quicklime about as large as split peas in the manner described on p. 12. Fit the end of the elbow-tube into the perforated cork of the drying tube, and support the flask in the Bunsen's holder¹ at such a height that the lamp will go easily underneath it.

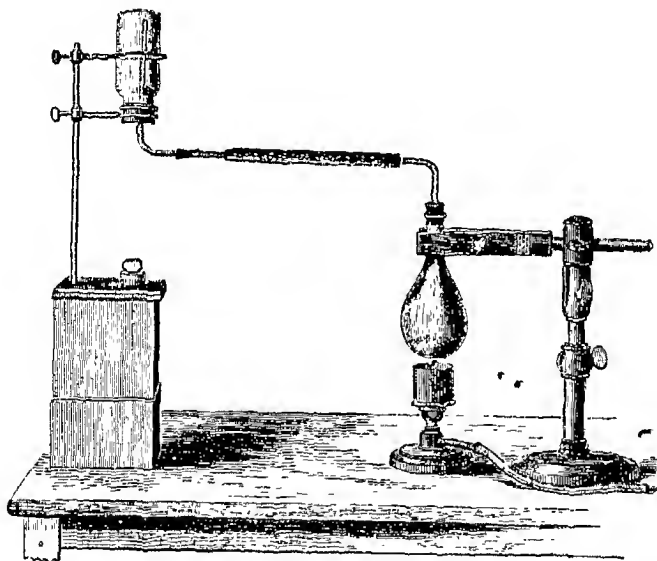


Fig. 76.

The ammonium chloride may now be taken from the sand-bath and set aside to cool; the cooling may be hastened by spreading it out on a sheet of paper.

Next, adapt a large flat cork to the smallest ring of the retort-stand, and bore a hole in it, through which the long

¹ A notch should be cut across the cork, near the end of each jaw of the holder (if this has not been done already), in order to grasp the neck of the flask more securely.

branch of the other elbow-tube should be passed so that its end may be about 12 cm. above the cork. Clamp the retort-ring in the position shown in the figure; one of the larger rings being fitted on above it, for the purpose of steadying the bottles while they are being filled. The retort-stand must now be supported on blocks at such a height that the drying tube may be horizontal when its end is connected with the elbow-tube by a short bit of india-rubber tubing, as shown in the figure.

The ammonium chloride will by this time have cooled, and should be mixed quickly and thoroughly with the quicklime in the mortar. The mixture should be shaken out on a half-sheet of paper and transferred at once to the flask, in the manner shown in fig. 52, p. 59 (the cork with elbow-tube being left resting on the Bunsen's holder).

Having restored the flask to its place and fitted the cork tightly into its neck, place one of the smaller bottles inverted over the up-turned end of the elbow-tube so that its mouth rests lightly upon the cork in the retort-ring (see the engraving). The flask may now be gently heated by the argand burner with a small flame, a piece of wire gauze being laid on the top of the chimney of the burner (for the first minute or two only), to distribute the heat.

[If a spirit lamp must be used, it should be moved to and fro under the flask, the flame being never allowed to rest in one place, otherwise the flask is apt to crack; an accident which is not unlikely to happen in any case, as the substance to be heated is a solid of low conducting power, and not a liquid, which would distribute the heat by convection.]

The chemical change which takes place is of the following kind.—Ammonium chloride consists of nitrogen, hydrogen, and chlorine; quicklime consists of calcium and oxygen. When the two substances are gently heated together, the calcium combines with the chlorine, and the oxygen takes all the hydrogen it requires to form water, while the rest of the hydrogen combines with the nitrogen to form ammonia.

The following diagram expresses the nature of the action,

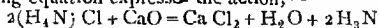
and shows also the exact weights of all the substances concerned.

Substances taken.	Composition.	Substances obtained.
Ammonium chloride, 107 parts	Nitrogen, 28 parts	28 } Ammonia,
	Hydrogen, 8 parts	6 } 34 parts.
	Chlorine, 71 parts	2 } Water,
Calcium oxide, 56 parts	Oxygen, 16 parts	16 } 18 parts.
	Calcium, 40 parts	71 } Calcium chloride, 40 } 111 parts ¹ .

While the bottle is being filled you may grease its stopper and those of the other bottles, and also fit a good cork to the neck of the large gas bottle, for use in expt. 5.

The gas comes off at a comparatively low temperature, and from its lightness collects in the highest part of the bottle, driving the air downwards before it, which will escape between the edge of the bottle and the cork. To ascertain when the bottle is full of gas, hold a piece of turmeric paper (moistened by being breathed upon) near its neck and slightly above its mouth. If the gas is overflowing, it will quickly and decidedly redden the test-paper. Remember, however, that a very little ammonia is sufficient to act on the paper; and hence it is advisable to leave the bottle in its place for about half a minute longer after the above effect has been observed, to ensure its being really full of gas. The bottle should then be slowly raised until clear of the delivery tube, and the stopper inserted at once. Another bottle may then be placed in the same position and filled in like manner². Fill four small bottles and

¹ The following equation expresses the action,—



The weight and volume of ammonia obtainable from the 15 grms. of ammonium chloride may be calculated on the principles already explained (see note, p. 120). The question is,—If 107 parts by weight of ammonium chloride yield 34 parts of ammonia, how much will 15 grms of the salt yield?

(1 litre of ammonia weighs 0.76 grm., nearly.)

² The same piece of turmeric paper may be used over and over again in testing for the gas; since, owing to the volatility of ammonia, the paper soon re-assumes its yellow colour.

one large bottle with the gas, then withdraw the lamp, disconnect the elbow-tube from the drying tube, and place the holder with the flask (still fitted with the cork and elbow-tube) in a draught-cupboard or in the open air.

[Before putting away the drying tube, the quicklime in it should be examined and any of it which appears slaked by the moisture should be taken out and thrown away. A bit of glass rod should then be put into the hole in the cork, and the other end of the tube stopped with a plug of cork, to prevent entrance of moisture.]

Properties of Ammonia.

***1. Its peculiar odour and its alkaline action on turmeric paper** will have been noticed already.

2. Its lightness has been sufficiently proved by its collection by upward displacement.

3. Its rapid diffusibility.

Place an empty gas jar, mouth upwards, on the table, and drop into it strips of wetted reddened litmus and turmeric paper. Bring over the mouth of the jar a small bottle of ammonia inverted, remove the stopper and place the mouths of the bottle and jar in contact for a few seconds. The gas, in spite of its low density, will diffuse downwards through the air; the reddened litmus will become blue and the turmeric red; thus showing at once the alkaline reaction of ammonia and its quick rate of diffusion.

4. Its relation to ordinary combustion.

Support a small bottle of ammonia on the smallest ring of the retort-stand (the cork being taken out) in the same position as when it was being filled. Withdraw the stopper and pass a lighted taper slowly up into the bottle. The taper will be extinguished, but the gas will show a tendency to burn with a greenish flame at the mouth of the bottle. The oxygen of the air, in fact, is just able (when heated) to decompose the ammonia, combining with its hydrogen but leaving its nitrogen nearly untouched.

[The feeble inflammability of ammonia in air may be shown by

restoring to its place the flask, fitted with elbow-tube, which was put aside just now, heating it so as to generate a little more ammonia, and bringing the flame of a Bunsen's burner close to the extremity of the tube from which the gas is issuing. A yellowish-green flame will be seen.]

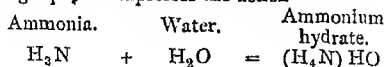
5. Its solubility in water.

Fill the supplementary pan of the pneumatic trough (or a basin) with water. Place a dry glass plate on the table, bring over it a small bottle of ammonia, mouth downwards, remove the stopper, and bring the mouth of the bottle at once down upon the glass plate. Then, still keeping the bottle inverted and the plate closely pressed against its mouth, plunge it below the surface of the water in the pan and withdraw the glass plate. The water will rise in the bottle, especially if the latter is gently shaken, and will fill it entirely if the gas is unmixed with air. There will usually be a small residue of air, and you will thus gain an idea how far you have been successful in filling the bottle by displacement.

The water in the bottle will be found to have gained the smell and alkaline reaction of the gas, and to have a caustic taste. It has, in fact, combined with the ammonia, not merely dissolved it, and the liquid is a solution of ammonium hydrate (the common 'solution of ammonia' which you will often have occasion to use in testing)¹.

[Another experiment illustrating the solubility of ammonia may be made, if time permits, as follows.—Take the cork which was recently fitted to the large gas bottle: bore a hole in the centre and fit into it a glass tube about 18 cm. long, ending in a jet (the pipette already made, p. 32, will do very well), so that the jet may project about 5 cm. within the bottle. Fill a beaker with water and add to it a few drops of solution of litmus together with one drop of dilute hydrogen chloride to make the litmus red. Twist a small piece of moistened tow round the tube just below the jet (this is for the purpose of beginning the absorption). Put the beaker

¹ The following equation expresses the action—



on the iron base of the retort-stand, and clamp one of the smaller retort-rings at such a height that when the neck of the bottle rests on it the end of the tube may reach nearly to the bottom of the beaker. Now invert the large bottle of ammonia, take out the stopper and quickly fit the cork into its place (still keeping the bottle inverted), and plunge the outer end of the tube into the beaker of coloured water, see fig. 77. The pressure of the external air will force the water up the tube, as the ammonia is absorbed and a vacuum made in the bottle, and a fountain will be formed, the red litmus becoming blue under the action of the ammonia.]

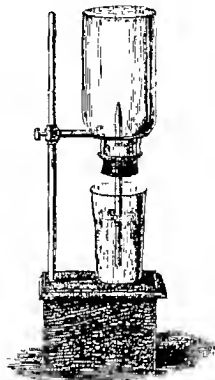


Fig. 77.

*6. Its combination with other radicles.

Ammonia shows a great tendency to combine directly with salts of hydrogen (*i.e.* the substances called acids), associating their hydrogen more closely with itself to form the radicle 'AMMONIUM,' containing 14 parts by weight of nitrogen combined with 4 parts of hydrogen (instead of with 3 parts, as in ammonia). Thus, when ammonia is brought into contact with hydrogen chloride the two gases combine to form the salt 'ammonium chloride'; the substance, in fact, from which you prepared the gas.

Dip a glass rod into strong hydrogen chloride and hold it just above the mouth of a bottle of ammonia, lifting the stopper for a moment only to let a little of the gas escape. White clouds of ammonium chloride will be formed when the gases mix.

[This reaction is very often made use of as a test for the presence of ammonia, and it is slightly preferable to use the strongest hydrogen acetate ('glacial acetic acid') instead of hydrogen chloride, since the latter itself gives slight white fumes in moist air, which might lead to a mistake.]

The nature and properties of ammonium salts will be more fully considered under AMMONIUM.

Additional Experiment.

Union of ammonia with oxygen, under the influence of platinum.

Platinum, as noticed under HYDROGEN, has a peculiar power of causing chemical combination: and when a piece of it is heated and put into a mixture of ammonia and air, the oxygen of the air combines with both the nitrogen and the hydrogen of the ammonia (and not with the hydrogen alone, as in expt. 4), with formation of an acid, hydrogen nitrite.

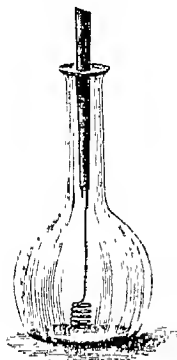


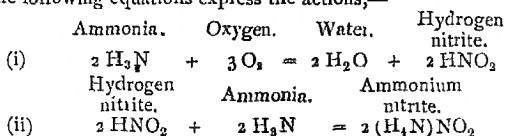
Fig. 78.

Form a piece of platinum wire, of the kind used for blowpipe experiments, about 15 cm. long, into a close spiral, by coiling it round a glass rod or pencil, and attach it to a strip of card sufficiently wide to fit rather tightly into the neck of a flask about 250 c.c. in capacity. The coil should hang down freely in the centre of the flask, about 1 cm. from the bottom, the card forming a diaphragm or partition vertically down the neck, as shown in fig. 78, and serving to divide the currents of gas and air.

Withdraw the coil from the flask, pour a few drops of a *strong* solution of ammonia into the latter, and shake it so as to diffuse the ammonia gas through the air contained in the flask. Heat the platinum spiral to redness in a Bunsen's burner, and while it is still red-hot plunge it into the flask. The coil will continue to glow for some time, and white fumes of ammonium nitrite will be almost immediately formed. The reason is this;—The hydrogen nitrite ('nitrous acid'), formed by the union of the hydrogen and nitrogen of the ammonia with the oxygen of the air, immediately combines with some of the undecomposed ammonia to form a solid salt, ammonium nitrite¹.

The use of the card partition in the neck will now be evident.

¹ The following equations express the actions,—



On one side of it a current of cold (and therefore heavy) air is descending into the flask, while on the other side the heated (and therefore lighter) vapours and gases are rising and escaping; thus affording a good illustration of 'convection-currents' in gases.

If, when the coil of wire has ceased to glow, the flask is gently heated by waving it for a few seconds at a little distance above a lamp flame, more ammonia gas will be evolved from the liquid, and the platinum will again become red-hot. After the lapse of a minute or two, take out the coil of wire, add 2 or 3 c.c. of water, and shake it up in the flask; then pour the liquid (which may be slightly yellow, owing to the presence of nitrogen tetroxide) into a test-tube, add enough dilute hydrogen sulphate to render the solution strongly acid to test-paper (when the smell of nitrogen oxides will be perceived), then add one drop of solution of indigo sulphate, and heat the mixture. The blue colour of the indigo will disappear, proving, under the conditions of the experiment, that a nitrite or nitrate is present (as hereafter shown, p. 160).

COMPOUNDS OF NITROGEN WITH OXYGEN.

Nitrogen forms five well-defined compounds with oxygen, a list of which is given below, and should be written out in the note-book. They or their compounds will be taken in descending order, beginning with compounds related to the oxide which contains most oxygen, nitrogen pentoxide.

List of the Nitrogen Oxides.

Name.	Composition by weight.		Salts related to them ¹ .	Examples.
	Nitrogen	Oxygen.		
Nitrogen pentoxide	28 parts :	80 parts	Nitrates	{ Hydrogen nitrate. Potassium nitrate.
„ tetraoxide	28 „ :	64 „	(none)	
„ trioxide	28 „ :	48 „	Nitrites	{ Hydrogen nitrite. Potassium nitrite.
„ dioxide	28 „ :	32 „	(none)	
„ monoxide	28 „ :	16 „	(none)	

[An account of the constitution and formulæ of the molecules of these oxides will be found in Appendix D. I.]

¹ By this it is meant that the salts mentioned can be obtained by the combination of the oxide with other substances, and that the oxide can be obtained from the salts.

6. NITRATES.

	Formula of molecule.
[Typical examples,—Hydrogen nitrate ('nitric acid')	HNO_3
Potassium nitrate ('nitre' or 'salt-petre')	KNO_3
Ammonium nitrate	$(\text{H}_4\text{N})\text{NO}_3$
Lead nitrate	$\text{Pb}(\text{NO}_3)_2$

These are substances which all contain as a common ingredient the NITRATE radicle, a substance composed of 14 parts by weight of nitrogen associated with 48 parts by weight of oxygen, which can be transferred from one of these compounds to another, but which has not yet been obtained in a separate form (see p. 85).

It has been seen in the last experiment (p. 154) that ammonia can be made to combine with oxygen to form a substance (a nitrite) which contains a radicle composed of nitrogen and oxygen. This oxidation of nitrogen goes on in nature on a large scale, during the decay or putrefaction of organic substances. The ammonia first formed is slowly oxidised to a nitrate; and thus soil is found to yield such salts as potassium nitrate ('nitre' or 'saltpetre'), and sodium nitrate; and it is from one or the other of these that the rest of the class of nitrates are usually obtained.

Preparation of Hydrogen nitrate.

Apparatus required —Stoppered (or plain) retort, about 200 c.c. in capacity; retort-stand; sand-bath with sand; argand, or spirit lamp; flask holding about 250 c.c.; porcelain mortar; Bunsen's holder; funnel, 10 cm. in diameter; beaker; test-tube stand; test-tubes in basket; watch-glass; washing bottle with distilled water; wooden blocks; blotting-paper; lamp cotton, or tow; cloth.

Solutions of barium chloride, silver nitrate, litmus, indigo sulphate, ammonium hydrate, iron protosulphate; crystallised potassium nitrate; common hydrogen sulphate; bit of worsted or flannel; white feather, from a quill pen; piece of thin sheet-lead; copper filings; charcoal.

Hydrogen nitrate (which is the common 'nitric acid' or 'aqua fortis') is generally prepared by heating a mixture of

potassium nitrate with hydrogen sulphate in a retort. Vapours of the acid are given off and may be condensed by cooling the neck of the retort in the same way as when water was distilled (Sect. I, Ex. 7).

Measure 20 c.c. of water into a beaker placed on a plate, and add to it by degrees 20 c.c. of strong common hydrogen sulphate. This should be done carefully, as great heat is evolved by the union of the acid with the water (compare the action of quicklime on water, p. 66) and the beaker may be broken. Add only about 1 or 2 c.c. at a time, and stir with a glass rod. When, however, the beaker has got pretty hot, all the rest of the acid may be added at once¹.

While the mixture is cooling, weigh out 20 grms. of potassium nitrate, powder the salt roughly in a mortar, and transfer it to the retort, in the manner shown in fig. 79.

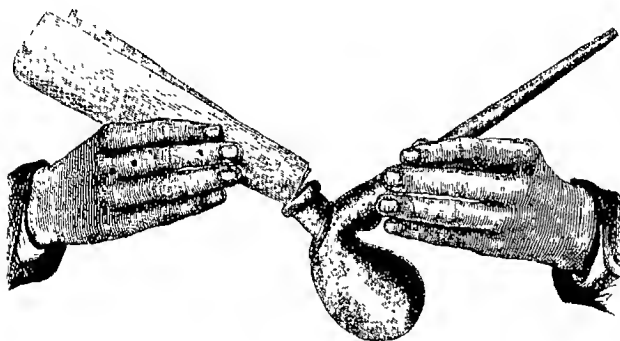


Fig. 79.

Arrange the retort on the sand-bath, precisely as for the distillation of water, p. 71, putting a small beaker temporarily in place of the flask as receiver, to collect the first portions of the distillate. Pour the diluted acid through the tubulure by means of a funnel, taking particular care that none of the liquid passes down the neck of the retort; then replace the glass stopper and proceed to heat the mixture at once, since there will be ample

¹ The mixture may be turbid, for a reason explained under SULPHATES.

time before any acid comes over to provide for the cooling and condensation of the vapour.

The condensing arrangement may next be set up, exactly as described on p. 71, since the acid obtained by using slightly diluted hydrogen sulphate, as above directed, has a higher boiling point than water, and is therefore easily condensed.

The action which goes on in the retort is a 'double decomposition' (see p. 83), which may be stated in the simplest form thus,—

Potassium nitrate with hydrogen sulphate

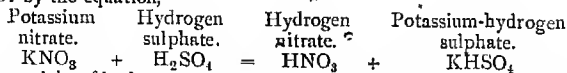
yield Hydrogen nitrate and potassium sulphate,

the potassium radicle changing places with the hydrogen radicle. But unless the temperature is very high only one-half of the hydrogen in the hydrogen sulphate is replaced by potassium, a salt called potassium-hydrogen sulphate being obtained. This is more exactly shown in the following diagram¹:—

Substances taken.	Composition		Substances obtained.
Potassium nitrate, 101 parts.	{ Nitrogen, 14 parts Oxygen, 48 parts Potassium, 39 parts	62 1 39	{ Hydrogen nitrate, 63 parts. Potassium-hydrogen sulphate, 136 parts.
Hydrogen sulphate, 98 parts.	{ Hydrogen, 2 parts Sulphur, 32 parts Oxygen, 64 parts	1 39 96	

When 2 or 3 c.c. of acid have distilled over remove the small beaker and substitute for it a flask as a receiver. The heat should be regulated so as to keep the liquid in the retort gently boiling.

¹ Or by the equation,—



The weight of hydrogen nitrate obtainable from the 20 grms. of potassium nitrate taken may be calculated in the manner already explained, the problem being,—If 101 parts by weight of potassium nitrate yield 63 parts of hydrogen nitrate, how much acid will 20 grms. yield?

You may also calculate in a similar way what weight of hydrogen sulphate is theoretically required for the decomposition of the 20 grms. of the salt; and, further, how much the acid you have taken is in excess of this quantity, assuming that the 20 c.c. of acid contain 37 grms. of real hydrogen sulphate.

While the distillation is going on, you may examine the purity of the acid which came over first, and was collected in the beaker. Add to it about 10 c.c. of distilled water, and divide the liquid between two test-tubes, pouring one-half into each.

(a) Test the first half of the solution with a drop of solution of barium chloride; shake the mixture and hold it up to the light. If a turbidity is perceptible, HYDROGEN SULPHATE is present as an impurity¹.

(b) To the other half of the solution add a drop of solution of silver nitrate. If a precipitate is produced, a CHLORIDE is present as an impurity, derived from the potassium chloride which the nitre of commerce usually contains.

When crystals make their appearance in the liquid and on the sides of the retort, put out the lamp, and, as soon as the apparatus has cooled a little, withdraw the receiver and reserve its contents for use in the following experiments.

[Leave the beak of the retort resting on the edge of the mortar until it is cold, so that no drops of the highly corrosive acid may fall on the table and do damage.

If any of the acid gets on the hands, clothes, or apparatus, pour on it at once some solution of ammonium carbonate as long as the addition causes effervescence, and then wash with plenty of water.

The residue in the retort consists of potassium-hydrogen sulphate, and may when cool be washed out with a little warm water. The retort itself, after being thoroughly rinsed with distilled water, should be set aside to dry, supported with the tubulure downwards in a Bunsen's holder or otherwise.]

Properties of Hydrogen nitrate.

The acid which you have prepared will be seen to be a nearly colourless liquid², perhaps giving off slight white fumes, as its vapour mixes with moist air, for a reason explained under

¹ It must be borne in mind that barium nitrate is insoluble in strong hydrogen nitrate; and hence if the solution of hydrogen nitrate is not very dilute, a crystalline precipitate may be formed. This, however, is easily distinguishable in appearance from barium sulphate, and will readily dissolve when more water is added, and the liquid warmed.

² It may be slightly yellow, owing to the presence of nitrogen trioxide and tetroxide, formed by the decomposition of the hydrogen nitrate which takes place if the temperature in the retort is somewhat too high.

HYDROGEN CHLORIDE (the concentrated acid, or 'aqua fortis,' fumes strongly), having a decided smell, very irritating when breathed, and a strongly acid taste. Its taste should be tried only after considerable dilution: one drop of the acid on a glass rod, mixed with 3 or 4 c.c. of water in a dish, may be used.

If time permits, the density of the acid may be taken by the method described on p. 50. It will be found to be decidedly higher than that of water.

***1. Its action on litmus.**

Put a little water into a test-tube, add enough solution of litmus to colour it strongly blue, and then add a drop of the acid. The blue colour will be at once changed to red, showing that hydrogen nitrate belongs to the class of substances which have an 'acid reaction.'

2. Its action on white wool, &c.

Put a bit of white worsted or flannel and the feather of a quill pen into a small porcelain dish, add a few drops of the acid, and warm gently. The substances will in a short time be stained yellow¹; but if the action is continued much longer they will be entirely destroyed. Treat a bit of calico or cotton wool in the same way: no yellow stain will be produced.

***3. Its action on indigo.**

Add one drop of solution of indigo sulphate to 5 c.c. of water in a test-tube: then add a few drops of hydrogen nitrate (observing that the acid does not turn *this* blue colouring matter red) and heat the mixture to boiling. The blue colour of the indigo will disappear, only a light brown colour remaining. This is due to the hydrogen nitrate giving up oxygen to the indigo with formation of a yellowish substance called 'isatin.'

Preparation of Ammonium nitrate.

You have already seen (p. 153) that ammonia unites directly with hydrogen chloride to form the salt called ammonium chloride. It unites in a similar way with hydrogen nitrate, forming

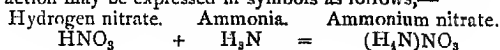
¹ If any of the acid gets on the fingers they will be stained a very permanent yellow.

ammonium nitrate. This salt has neither the acid reaction of hydrogen nitrate nor the alkaline reaction of ammonia, but is neutral to test-paper.

Pour 5 c.c. of the hydrogen nitrate into a porcelain dish, and add about 3 c.c. of solution of ammonia (ammonium hydrate). Stir the mixture with a glass rod, and place the drop of it which adheres to the rod upon a strip of blue litmus-paper laid on a clean white plate, drawing a thin line across the strip. The liquid will redden the litmus-paper decidedly. Continue to add ammonia cautiously drop by drop, stirring the mixture, and placing a fresh drop from time to time on an untouched part of the strip of litmus-paper. You will find that a time will arrive when the liquid no longer alters the colour of the blue litmus-paper. When this is the case, place a drop of it on a piece of reddened litmus-paper, and observe whether the red colour is changed to blue. If so, pour about 1 c.c. of the hydrogen nitrate into a test-tube, dilute it with about five times its volume of water, and add it by means of a pipette drop by drop to the solution in the dish, stirring thoroughly after each addition and constantly trying the action of the liquid on both blue and reddened litmus-paper. This operation is called 'neutralising' a solution, and is frequently used in qualitative analysis. You will eventually obtain a solution which does not materially alter the colour of either test-paper, and is, in fact, neutral: although we know that hydrogen nitrate has an acid- and ammonia an alkaline-reaction. The two substances have, in fact, combined to form a single salt, ammonium nitrate, which has, as above stated, no action on test-paper¹. Observe in what exact and definite proportions the two substances combine; a single drop too much of either showing its presence by its action on the litmus.

Evaporate the solution on the sandbath at a moderate heat, taking away the lamp as soon as white fumes begin to appear (otherwise the salt will be decomposed). For the sake of comparison, evaporate also to dryness, on separate watch-glasses, a

¹ The action may be expressed in symbols as follows,—



little hydrogen nitrate and a little ammonia: taking care not to put the watch-glasses very near each other. You will find that a white residue will be left in the porcelain dish, while there will be scarcely a trace of a residue left in the watch-glasses.

The result of this experiment proves that, by bringing hydrogen nitrate into contact with ammonia in a certain definite proportion, a substance, ammonium nitrate, is obtained which differs from them in at least two respects, (*a*) in having no action on vegetable colours, (*b*) in being a crystallisable solid at ordinary temperatures.

Preparation of Lead nitrate.

Put about 1 grm. of thin sheet-lead (the lead foil used for lining tea chests answers well) into a porcelain dish, pour upon it 8 or 10 c.c. of hydrogen nitrate, and heat it on a sandbath (in a draught-cupboard, if possible, as the fumes are corrosive and poisonous).

The chemical change is of the following kind:—the lead displaces hydrogen from the hydrogen nitrate (as zinc was found to displace hydrogen from hydrogen chloride, p. 80), forming lead nitrate. But the hydrogen in this case is not given off as gas; it acts on some of the remaining hydrogen nitrate, taking away so much oxygen from it that lower nitrogen oxides are evolved in the form of orange vapours. The metal will soon dissolve¹, and the solution should be evaporated to complete dryness, when lead nitrate will be left as a white residue, and should be kept for making nitrogen tetroxide, Ex. 7.

This is an example of a very common and important use of hydrogen nitrate: *viz.* in the preparation of other nitrates by the replacement of its hydrogen by another radicle. Nearly all the metals, as will be seen in Sect. III, act on it with formation of soluble salts. Copper, for instance, as will be almost immediately proved (in preparing nitrogen dioxide), forms copper nitrate; silver forms silver nitrate ('lunar caustic'): and so on.

¹ It is hardly necessary to remark that in most cases where a substance is said to 'dissolve in' an acid, the phenomenon really consists in the formation, by the action of the acid, of a salt soluble in water.

General Properties of Nitrates.

[For the following experiments crystallised potassium nitrate and a solution of the same salt (made by dissolving 0.5 gm. in 25 c.c. of distilled water¹) should be used. In order to make the solution quickly, place the proper quantity of the salt in a glass mortar, grind it to powder, then add 2 or 3 c.c. of water, and grind the whole together. Pour off the liquid into a large test-tube, add a little fresh water to the residue in the mortar, and again grind the whole together and decant the solution. In this way, by several successive triturations with fresh quantities of water, the whole of the salt will soon be obtained in solution, and the liquid should then be put into a measure and made up to the required volume.]

*1. They give up oxygen readily.

Put a small crystal of potassium nitrate into an ignition tube (fig. 42, p. 42), add a splinter of charcoal, and heat over a Bunsen's burner. The salt fuses, and when the charcoal becomes red-hot a vivid deflagration will take place, owing to the decomposition of the nitrate and oxidation of the charcoal; the oxygen uniting with the potassium and some of the carbon to form potassium carbonate, and with the rest of the carbon to form carbon dioxide, which is given off together with nitrogen gas.

This illustrates one of the great uses of potassium nitrate, viz. in the manufacture of gunpowder, which is merely an intimate mixture of potassium nitrate, charcoal, and sulphur. The force of the explosion of gunpowder depends on chemical actions similar to that just described; the nitrate giving up oxygen not only to the charcoal but also to the sulphur, with formation of a large volume of gases.

*2. They destroy the blue colour of indigo.

Pour 3 or 4 c.c. of water into a test-tube, and add about half its volume of strong pure hydrogen sulphate, dropping in the acid little by little, lest the tube should be broken by the heat evolved. Next, add just sufficient solution of indigo sulphate to

¹ In cases where, as here, a solution of salt is prepared for the purpose of being tested, the strength of the solution is such that 50 c.c. of it would contain (approximately) a weight corresponding to that of a molecule of the substance, expressed in centigrammes. See Appendix B.

colour the liquid distinctly blue, and heat the mixture to boiling. The blue colour of the indigo will remain unaltered, if the acid is pure (see note ¹).

Now add a few drops of the solution of potassium nitrate and boil again. Hydrogen nitrate will be formed by the same double decomposition as in the preparation of the acid, p. 158, and the blue colour of the indigo will disappear entirely, for the reason already explained, p. 160.

***3 They are acted on by copper, with formation of lower nitrogen oxides.**

Pour into a test-tube 2 or 3 c.c. of the solution of potassium nitrate; add an equal volume of strong hydrogen sulphate, drop in a bit of copper wire (or, better, copper filings) and warm gently. Nitrogen dioxide will be given off, and may be recognised by the orange vapours which it forms with the oxygen of the air in the tube. These may be most distinctly seen by placing the tube on a piece of white paper and looking down into it. The chemical change will be more fully explained under NITROGEN DIOXIDE.

***4. They act on iron protosulphate, with formation of a brown compound.**

Place a little solution of potassium nitrate in a tube, add an equal volume of hydrogen sulphate as in the last experiment, and cool the mixture by holding the test-tube in a stream of water. Then, holding the tube in a slanting position, pour as slowly as possible down the side (most conveniently from a pipette) a solution of iron protosulphate, so that the lighter solution may not mix with, but float upon, the heavier; and leave the tube undisturbed in the test-tube stand for a few minutes. A dark brown ring will eventually be formed at the line of junction of the two liquids, which will be best seen by raising the test-tube to a level with the eye and holding a piece of white paper behind it. In this case the nitrate has given up

¹ Hydrogen sulphate is liable to contain nitrates, in which case the blue colour of the indigo will disappear. If so, add another drop or more of indigo sulphate, until the liquid remains blue even on boiling.

oxygen to the iron protosulphate, with formation (as in the last expt.) of nitrogen dioxide. This latter combines with the excess of iron protosulphate to form the brownish-black compound.

If the mixture in the tube is now heated, the dark stratum will disappear with effervescence due to the liberation of nitrogen dioxide.

This is a very characteristic test for the presence of nitrates: and it also illustrates the principle of a good method of preparing nitrogen dioxide (p. 173).

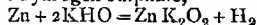
Additional Experiment.

Reduction of nitrates by nascent hydrogen, with formation of ammonia.

When hydrogen is just in the act of being liberated from a compound, or is 'nascent,' as it is called, it shows unusually strong powers of acting on and combining with other substances. For instance, it will, under these circumstances, decompose nitrates, combining (*a*) with their oxygen to form water, (*b*) with their nitrogen to form ammonia.

Put about 2 grms. of caustic potash (potassium hydrate) into a test-tube, add 5 c.c. of water, and shake until the potash is dissolved; then drop in two or three small pieces of granulated zinc, add one drop of solution of platinum perchloride and warm gently, supporting the tube on wire gauze laid on a ring of the retort-stand; the smallest retort-ring being placed round the tube to hold it upright. Hydrogen gas will be evolved¹, and may be recognised by covering the mouth of the tube with a bit of paper or card to confine the gas, and after a few seconds introducing a lighted match into the tube. Hold a piece of moist reddened litmus-paper at the mouth of the tube: no change of colour will be observed, if the potash is pure. (If the paper turns blue there must be some nitrogenous impurity in the potash, and the boiling must be continued until the vapours cause no change of colour in the test-paper.) Now drop in a small crystal of potassium nitrate, keeping

¹ The zinc replaces hydrogen in acting upon potassium hydrate, precisely as it does in acting upon hydrogen sulphate,



The platinum reduced as a black powder upon the zinc promotes the action by forming with the zinc a galvanic couple (compare the galvanic action between zinc and platinum in the experiment illustrating analysis by electricity, p. 79).

the mixture heated. Ammonia will very shortly be formed, and may be recognised by its odour and its action on a piece of reddened litmus-paper held at the mouth of the tube.

From the nitrates all the nitrogen oxides can be obtained. Thus hydrogen nitrate may by the action of phosphorus pentoxide be separated into nitrogen pentoxide and water; the process, however, is neither easy nor safe enough for the beginner to attempt. All the other oxides can be obtained by withdrawing the proper quantity of oxygen from a nitrate, and they will be prepared and examined in due order.

7. NITROGEN TETROXIDE.

[Formula of molecule, N_2O_4

Weight ,, 92 hydrogen-atoms.]

Apparatus required.—Bunsen's holder; argand burner; test-tube about 1.5 cm. in diameter; retort-stand; sand-bath; lead nitrate (already prepared, p. 162); test-papers; cork to fit test-tube.

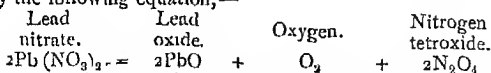
Preparation of Nitrogen tetroxide.

The nitrate usually employed to obtain this oxide is lead nitrate, which when heated gives off a mixture of nitrogen tetroxide and oxygen.

Scrape together the residue of lead nitrate which you obtained by dissolving lead in hydrogen nitrate (p. 162), and heat it in the dish on a sand-bath, stirring it constantly, until it is thoroughly dry. Then put it into a moderate-sized test-tube supported in the Bunsen's holder (as in fig. 62, p. 77), and heat it pretty strongly over an argand burner. A deep orange vapour will be given off, which is nitrogen tetroxide.

The chemical change is expressed by the following diagram¹.

¹ Or by the following equation,—



The presence of oxygen in the tube may be shown by introducing a glowing match (nitrogen tetroxide itself having no tendency to support combustion).

Substance taken.	Composition.	Substances obtained.
Lead nitrate, 331 parts.	Lead, 207 parts	207 } Lead oxide, 223 parts.
	Oxygen, 96 parts	16 }
	Nitrogen, 28 parts	16 } Oxygen, 16 parts.
		64 } Nitrogen tetroxide, 92 parts.
		28 }

Properties of Nitrogen tetroxide.

1. Its deep orange colour has been already noticed. This becomes much more intense when the gas is heated, as may be shown by heating the lower half of the tube more strongly. After the next experiment has been tried, allow the tube to cool, closing its mouth loosely with a cork; observe that the vapour becomes much paler in colour as it cools.

2. Its action on water, forming acids.

Nitrogen tetroxide combines readily with water, forming two acids, hydrogen nitrate and hydrogen nitrite. To prove this, moisten a piece of blue litmus-paper with distilled water, and dip it into the tube; it will be strongly reddened.

8. NITROGEN TRIOXIDE.

[Formula of molecule, N_2O_3

Weight „ 76 hydrogen-atoms]

Apparatus required.—Retort-stand; wire gauze; argand burner; test-tube, about 1.5 cm. in diameter; china plate; test-papers; blotting-paper.

Starch; strong hydrogen nitrate; solution of potassium hydrate; distilled water.

Preparation of Nitrogen trioxide.

This gas is obtained, though not in a pure condition, by the action of starch on hydrogen nitrate.

Put a little starch (about as much as will lie on the end of a

spatula) into a test-tube, add about 3 drops of water and mix it with the starch by a thorough shaking. Then add 3 c.c. of strong hydrogen nitrate, mix the whole thoroughly, and heat it cautiously, supporting the tube on wire gauze placed on a ring of the retort-stand, and placing the smallest retort-ring round the tube to hold it upright. The lamp should be removed as soon as an effervescence begins. The liquid will turn yellow, and orange vapours of nitrogen trioxide, resembling in colour those of the tetroxide, will be given off.

The chemical change is rather complicated, but the general nature of it is that the carbon and hydrogen of the starch take away some oxygen from the hydrogen nitrate, leaving enough combined with the nitrogen to form nitrogen trioxide.

Properties of Nitrogen trioxide.

1. Its orange colour has been noticed already. It does not vary in intensity with the temperature like that of the tetroxide.

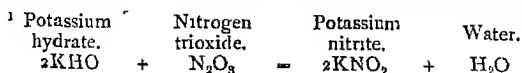
2. Its action on water, forming hydrogen nitrite.

Moisten a piece of blue litmus-paper, and introduce it into the tube. It will be strongly reddened, as the gas combines with the water to form hydrogen nitrite ('nitrous acid').

3. Its combination with potassium hydrate.

Nitrogen trioxide unites with most oxides or hydrates of metals, forming a class of salts called NITRITES (the termination -ITE implies that the radicle contains less oxygen than that with the termination -ATE, *viz.* the NITRATE radicle), of which potassium nitrite may be taken as an example.

Fold a small piece of blotting-paper into a strip narrow enough to go into the test-tube, lay it on a plate and moisten it with a few drops of solution of potassium hydrate; then introduce it into the tube filled with the vapours of nitrogen trioxide. The vapours will be quickly absorbed by the potassium hydrate (as proved by the complete disappearance of the orange colour in that part of the tube), with formation of potassium nitrite¹.



Additional Experiments.

Properties of Nitrites.

[Typical examples,—Hydrogen nitrite, HNO_2
Potassium nitrite, KNO_2]

[For use in the following experiments 0.5 gm. of potassium nitrite¹ should be dissolved in 30 c.c. of water, as directed in the case of potassium nitrate, p. 163.]

Nitrites are remarkable as showing both 'oxidising' and 'reducing' powers: *i.e.* they show a tendency, not only to give up some of their oxygen to other things, but also to take away oxygen from substances capable of yielding it.

1. Oxidising properties of nitrites.

(a) They destroy the blue colour of indigo.

Make a strongly acid solution of indigo precisely as directed in expt. 2, p. 163; add to it a few drops of the solution of potassium nitrite, and boil the mixture. The blue colour of the indigo will disappear as in the case of the nitrates, and for a similar reason, *viz.* that the nitrite gives up oxygen to the indigo.

(b) They oxidise iron protosulphate, with formation of nitrogen dioxide.

Pour 3 or 4 c.c. of solution of iron protosulphate into a test-tube, add about half as much strong hydrogen sulphate, and cool the mixture in a stream of water. Then add a little of the solution of potassium nitrite. The liquid will turn brownish-black, and on being heated will give off nitrogen dioxide and become light yellow. The action is precisely similar to that already explained in the case of nitrates (see expt. 3, p. 164), but it takes place much more readily with nitrites.

In the above two experiments nitrites are seen to resemble nitrates; but in the experiments which follow they will be shown to differ considerably from the latter.

* (c) They liberate iodine from hydrogen iodide.

Put a few drops of solution of potassium iodide into a test-tube, add about 10 c.c. of water and five or six drops of dilute hydrogen

¹ Or, if no potassium nitrite is at hand, the strip of blotting-paper on which potassium nitrite was formed in the last experiment, together with a couple of other pieces similarly treated (being left for a minute or more in the stream of nitrogen trioxide) may be put into a beaker and stirred up with about 10 c.c. of water to dissolve the potassium nitrite.

sulphate. The liquid now contains hydrogen iodide, formed by double decomposition¹.

Add to this a drop of the solution of potassium nitrite; iodine will be at once liberated, colouring the liquid yellow².

In this action, the nitrite has given up oxygen to the hydrogen of the hydrogen iodide; water being formed and iodine liberated.

[Compare this result with the action of nitrates; which, though they contain more oxygen than nitrites, do not give it up so readily.

Make a little more solution of hydrogen iodide, as above directed, and add a drop or two of solution of potassium nitrate. No immediate liberation of iodine will be observed. Hence this reaction may be used to distinguish between nitrites and nitrates.]

2. Reducing properties of nitrites.

This is best seen in the manner in which they separate mercury from its salts.

Pour some solution of potassium nitrite into a test-tube, and add a drop of solution of mercury protonitrate³. A gray precipitate of metallic mercury will be produced; the metal having been 'reduced' (an old alchemical term) from its combination with the nitrate radicle, while the potassium nitrite is converted into potassium nitrate⁴.

*3. Formation of hydrogen nitrite, and its instability.

When hydrogen sulphate is added to a nitrite, hydrogen nitrite is formed by double decomposition (as with nitrates, p. 158). But this body immediately breaks up into (a) a substance containing more oxygen, *viz.* hydrogen nitrate, (b) a substance containing less oxygen, *viz.* nitrogen dioxide.

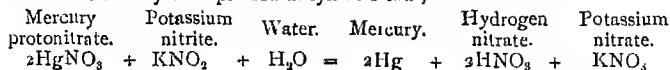
¹ Hydrogen sulphate and potassium iodide give potassium sulphate and hydrogen iodide. Compare the change which occurs in the preparation of hydrogen nitrate.

² The presence of free iodine may be confirmed by the characteristic blue colour formed on addition of solution of starch (see under IODIDES).

³ If none of this is at hand (it is a reagent seldom required), a little may be made by putting a small globule of mercury into a test-tube, adding a few drops of water and then about twice as much strong hydrogen nitrate. The action may be started by warming the mixture, but it should not be allowed to go on so far as to dissolve the whole of the metal.

⁴ It should be noted that water takes part in the action. In fact the potassium nitrite takes the oxygen, which it requires to form potassium nitrate, from the water present; leaving the hydrogen of the water free to displace mercury from its combination with the nitrate radicle.

The action may be expressed in symbols thus,—



Pour 3 or 4 c.c. of the solution of potassium nitrite into a test-tube and add about half as much strong hydrogen sulphate. An effervescence will occur (especially if the solution is warmed) due to the escape of nitrogen dioxide, which will form orange vapours by combining with the oxygen of the air in the tube¹.

9. NITROGEN DIOXIDE.

[Formula of molecule, N_2O_2

Weight „ 60 hydrogen-atoms.]

Apparatus required.—Pneumatic trough; flask, fitted with the delivery tube and funnel used in Ex. 2; retort-stand; wire gauze; glass measure; beaker; one large and three small gas bottles; two gas jars, 20×5 cm.; one ditto, 10×3 cm.; taper on wire; glass disc; test-tubes and stand; blue litmus-paper; india-rubber rings.

Copper clippings; strong common hydrogen nitrate; solution of iron protosulphate; carbon disulphide; bottle of oxygen (unless a supply can be obtained from a gas-holder).

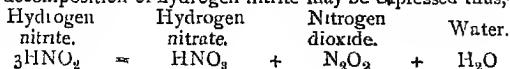
Preparation of Nitrogen dioxide.

This oxide is formed when copper is made to act upon hydrogen nitrate, as in Experiment 3, p. 164. It is, unlike the other nitrogen oxides, insoluble in water, and hence can be collected over the pneumatic trough in the usual way.

Measure out 50 c.c. of water and place it in a beaker large enough to hold more than twice the quantity; then measure out the same volume of strong (common) hydrogen nitrate and add it to the water in the beaker. Notice the heat evolved (due to the chemical combination of the water and the acid), which is not, however, so great as that produced by the union of hydrogen sulphate and water, p. 157.

Place in the flask about 30 grms. (10 or 12 strips about 0.5 cm. broad and 5 or 6 cm. long) of sheet copper, and arrange the apparatus precisely as was done in preparing hydrogen, fig. 72, p. 126. Pour a little water into the flask, but only *just* sufficient to cover the end of the funnel, and try whether the

¹ The decomposition of hydrogen nitrite may be expressed thus,—



joints are tight as directed on p. 126. Fill the gas bottles and jars with water and place them inverted on the shelf of the trough, the stopper of each being placed upon its own bottle, to prevent confusion. When everything is ready pour the diluted acid into the flask. An effervescence will almost immediately commence, and the flask will be filled with orange vapours, which are not, however, nitrogen dioxide, but one of the higher oxides formed by the union of the dioxide with the oxygen of the air in the flask. These will be soon absorbed by the water, so that the column of water in the delivery tube will rise a little and no permanent gas will come over at first. If there is little or no action after the lapse of a minute, the acid may have been too much diluted, and about 2 or 3 c.c. of strong acid may be poured into the flask. A colourless gas will shortly come over, with which, after rejecting two jars full, the bottles and jars may be filled for experiments.

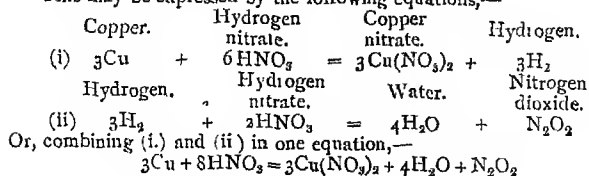
The reaction is of the following nature:—

1. Copper displaces hydrogen in a portion of the acid, forming copper nitrate.

2. The displaced hydrogen, instead of being evolved as gas, acts upon another portion of hydrogen nitrate, combining with some of its oxygen, while the nitrogen and the rest of the oxygen are evolved as nitrogen dioxide¹.

No heat is required at first to accelerate the action: indeed, it may become too violent, and should then be moderated by surrounding the flask with a wet cloth or moistened blotting-paper. On the other hand, if the evolution of gas becomes slow before the receivers are all filled, 1 or 2 c.c. of strong acid should be added through the funnel. When sufficient gas has been collected, the retort-stand and flask should be taken away

¹ This may be expressed by the following equations,—



at once, and placed in the open air. The blue liquid is, of course, a solution of copper nitrate, and will hardly be worth preserving.

[Reserve one small bottle of nitrogen dioxide for use in the next exercise.]

[Besides the process above given, the following is an excellent method of obtaining pure nitrogen dioxide. Measure 80 c.c. of water and place it in a beaker large enough to hold twice the quantity. Measure 30 c.c. of strong (common) hydrogen sulphate, and add it, little by little (see p. 157), to the water in the beaker, stirring the mixture with a glass rod. When all the acid has been added, place the beaker aside to cool. Meanwhile, weigh out 10 grms. of potassium nitrate and 100 grms. of iron protosulphate. Arrange an apparatus as above directed, and place the mixture (in crystals, not powder) in the flask, adding about a teaspoonful of sand, to make the action regular. Pour on it the diluted acid through the tube-funnel, and apply a gentle heat to the flask, watching carefully for the first signs of evolution of gas, and taking away the lamp temporarily if a rush of gas commences. The mixture will become brown, and pure nitrogen dioxide will be evolved. The general nature of the action will be evident from an experiment already made in examining nitrates (see p. 164, Expt. 4). The iron protosulphate takes away oxygen from the nitrate, with formation of nitrogen dioxide. This, owing to the heat applied, does not combine with the iron salt (as in the experiment above alluded to) but is given off as gas².]

Properties of Nitrogen dioxide.

The striking points of difference between this gas and the other nitrogen oxides should be carefully noted. It stands apart from the other members of the series in a way which has not yet been fully explained.

1. It is colourless and insoluble in water.

These characters will have been noticed already. If it had any action on water, like the other oxides, it could not have been collected over the pneumatic trough.

2. It has, when pure, no action on litmus-paper.

Attach a strip of blue litmus-paper to a glass rod by means of

¹ $6\text{FeSO}_4 + 4\text{H}_2\text{SO}_4 + 2\text{KNO}_3 = 3\text{Fe}_2(\text{SO}_4)_3 + 4\text{H}_2\text{O} + \text{K}_2\text{SO}_4 + \text{N}_2\text{O}_2$

an india-rubber ring (cut from a piece of tubing); and pass it up into one of the jars of gas standing on the shelf of the trough, taking care that no air enters. The colour of the litmus will remain unchanged¹.

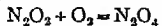
[Leave the litmus-paper in the jar, for the next experiment.]

3. It readily combines with free oxygen.

(a) Raise the mouth of the jar of gas in which the litmus-paper has been placed, for a moment above the water, so as to allow a little air to enter. Orange vapours will be formed, and the litmus-paper will be at once turned red. The explanation is that nitrogen dioxide, though a neutral substance itself, unites with the oxygen of the air, producing one of the higher nitrogen oxides, which (as has been seen) combines with water to form an acid. The action will be more closely examined in the next experiment.

(b) Refill with water the jar used in the last experiment, and decant into it one measure of oxygen, using the small cylindrical jar as a measure. Fill the small jar with nitrogen dioxide, and decant its contents, bubble by bubble, into the oxygen. Orange vapours of nitrogen tetroxide will be at once formed, and the bulk of the mixed gases, which will be at first slightly increased owing to the heat produced by their union, will soon diminish, as the tetroxide dissolves in the water, until only about one-half of the original volume of oxygen remains. Add in the same way another measure of nitrogen dioxide; stopping, however, if the addition of a bubble no longer causes the formation of orange vapours. Eventually, if the oxygen and nitrogen dioxide were pure, no residue of permanent gas will be left. Hence we learn that two volumes (or 60 parts by weight) of nitrogen dioxide combine with one volume (or 32 parts by weight) of oxygen, to form nitrogen tetroxide².

¹ A slight acid reaction may appear, if even a trace of air has been allowed to enter with the paper. If so, make the paper strongly blue by holding it close to the mouth of a bottle of solution of ammonium hydrate, and put it again into the jar.



² It should be observed that the formulæ N_2O_2 and N_2O_4 represent weights

4. It does not support ordinary combustion, or burn itself.

Insert the stopper into one of the small bottles of gas, remove the bottle from the trough, and place it mouth upwards on the table. Plunge into the gas the taper, lighted; it will be immediately extinguished, and the gas will not take fire¹.

[The stoppers should *not* be re-inserted into the bottles of the gas which have been used for this and other experiments, lest they should become immovably fixed by the pressure of the air, owing to the vacuum caused by the absorption of the nitrogen tetroxide by the moisture in the bottle.]

5. It will give up oxygen to some substances; e.g. carbon disulphide.

It has been proved in Experiment 3 that nitrogen dioxide has a great tendency to combine with more oxygen. But it can also be made to give up the oxygen it contains (although, as just now observed, a taper will not effect this) by the action of substances possessing a strong affinity for oxygen, such as carbon disulphide.

Pour into a small dry test-tube about 2 c.c. of carbon disulphide, and place it in the stand, within reach (taking care that no lighted lamp is near, since carbon disulphide is highly combustible). Place one of the larger cylindrical jars of nitrogen dioxide on the table, previously decanting into it, if necessary, a few bubbles of gas, so as to fill it completely. Slide the glass cover aside for a moment, and pour the carbon disulphide quickly into the jar (taking care to admit as little air as possible); shake it up quickly, to diffuse the vapour through the gas, replace the jar on the table, and apply a lighted match to its mouth. No explosion will follow, but a brilliant flash of bluish light will pass down the jar. The oxygen of the nitrogen dioxide

of the gases which occupy twice the space of the usual unit of volume, *viz.* the volume occupied by the weight of hydrogen expressed by the formula H_2 . For a fuller account of this anomaly a theoretical text-book must be consulted.

¹ The taper sometimes, if in full combustion and if the gas contains a little nitrogen monoxide (as it is liable to do when made by this method), continues to burn, and with increased brilliancy.

unites with both the carbon and the sulphur of the carbon disulphide, forming carbon dioxide and sulphur dioxide, while the nitrogen remains uncombined¹.

6. It combines with iron protosulphate.

Place 4 or 5 c.c. of solution of iron protosulphate in a test-tube, add 6 or 8 drops of dilute hydrogen sulphate, and pour it into a small jar of the gas. Close the mouth of the jar with a glass plate, and agitate the liquid. A dark-brown solution will be formed, which, when poured into a test-tube and boiled over a lamp, will give off the gas with effervescence, becoming nearly colourless again.

This explains some results noticed in previous experiments (p. 164, Expt. 4, and p. 169), which were really due to the formation of nitrogen dioxide, as there stated.

Additional Experiment.

It was shown in Expt. 3 that nitrogen dioxide will combine with free oxygen, forming a higher nitrogen oxide, which readily dissolves in water. It is easy to infer that this substance might be used instead of phosphorus to determine the amount of oxygen in air; and, in fact, the first accurate analyses of air were made on this principle by Cavendish, about a century ago.* The following experiment will serve to illustrate his mode of proceeding:—

Take one of the larger cylindrical gas jars, and graduate it into five equal parts in the way described on p. 142. Fill it to the fifth division with air, as there directed; then fill the small measure with nitrogen dioxide, and decant the gas gradually into the air enclosed in the graduated jar. Add one more measure of nitrogen dioxide in the same way; you will then have added two volumes of nitrogen dioxide to five volumes of air. Now agitate the graduated jar (taking care that its mouth is not raised above the surface of the water in the trough), in order that the higher nitrogen oxides may be entirely absorbed; leave it to cool undisturbed for a few minutes; and, finally, depress it in the trough until the water inside and outside stands at the same level, and note the volume of the residual gas. It will be approximately four-fifths of the original volume of air, and if no further red fumes are formed on addition

¹ A portion of the sulphur is also separated and appears as a yellow deposit on the sides of the jar.

of a little more nitrogen dioxide, we may assume that the oxygen of the air is entirely removed, and consequently that five volumes of air contain approximately one volume of oxygen. The residual gas may be tested with a lighted taper and shown to be a non-supporter of combustion; further tests would absolutely prove it to be nitrogen.

10. NITROGEN MONOXIDE.

[Formula of molecule, N_2O

Weight „ 44 hydrogen-atoms.]

Apparatus required.—Pneumatic trough, to be filled with warm water; stoppered retort, with long beak; retort-stand; piece of wire gauze; argand burner; scales and weights; deflagrating cup; two gas jars, 20×5 cm.; one ditto, 10×3 cm.; one gas bottle, holding 700 c.c.; three ditto, holding 200 c.c.; taper on wire; glass disc; cedar spills; sheet of writing-paper.

Ammonium nitrate, in crystals; sulphur; bottle of nitrogen dioxide.

This is the lowest in the series of nitrogen oxides, containing less oxygen than any other. It is usually prepared by heating ammonium nitrate, a salt of which the formation has been already illustrated on p. 161. The gas is, as will be seen, rather soluble in water, but much less so when the water is heated; hence it may be collected without much loss over the pneumatic trough filled with warm water.

Preparation of Nitrogen monoxide.

Fill the pneumatic trough partly with cold water, and add sufficient boiling water to make the whole lukewarm.

Weigh out 20 grms. of ammonium nitrate, and transfer it to the retort in the manner shown in fig. 79, p. 157. Support the latter on a piece of wire gauze bent into the form of a dish, and placed on the largest ring of the retort-stand in such a position that the beak may dip under the shelf of the pneumatic trough, and that there may be room for the argand burner under the wire gauze. If the beak of the retort is inconveniently short, it may be lengthened by attaching a bit of glass tube of

the same size by an india-rubber connector. In order to keep the retort steady, the smallest ring may be brought down over the tubulure, and to do this it will be most convenient to arrange the retort-stand so that its stem is *behind* the retort, as shown in fig. 59, p. 71¹.

Heat the retort (slowly at first) by a lamp, and while it is gradually becoming hot, fill the gas jars and bottles with water, and place them, mouths downwards, on the shelf of the trough. The salt will soon fuse into a clear liquid, and by a slight increase of the heat will begin to decompose with effervescence owing to the escape of nitrogen monoxide. Be careful not to use more heat than is necessary to keep the fluid steadily effervescing, and do not, on the contrary, withdraw the lamp entirely while the beak of the retort is under water; or the sudden condensation of the steam, which is one of the products of the decomposition, will be likely to draw up water from the trough into the hot retort, and crack it. When the evolution of gas begins, white fumes (consisting of particles of the salt tossed up as spray by the escaping gas) will appear in the retort. So long as these are formed only in moderate quantity no harm need be apprehended; but if they increase, and the effervescence becomes violent, the heat should be diminished (not withdrawn) at once.

[The inconvenience of using too high a temperature in decomposing ammonium nitrate may be illustrated by heating a small fragment of the salt in an ignition tube. If the heat is rather quickly raised, the decomposition will become so rapid as to cause a slight explosion, with a yellowish flame.]

The decomposition of ammonium nitrate by heat is of the following nature. It contains hydrogen, nitrogen, and oxygen; the hydrogen unites with some of the oxygen to form water,

¹ It is a decided advantage to use a retort instead of a flask and delivery tube, in the preparation of this gas. If the latter is used, the water which is formed in the reaction collects in the neck, and drops down on the melted salt, producing a burst of vapour. The retort can be more uniformly heated, and the water which condenses in the neck flows down into the trough; moreover the beak of the retort is wider than the usual delivery tube, and hence the condensation of the water is more regular.

while the nitrogen associated with the rest of the oxygen forms nitrogen monoxide.

[Thus,

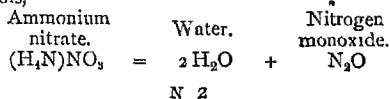
Ammonium nitrate, 80 parts.	{	Nitrogen, 28 parts	28	{	Nitrogen monoxide, 44 parts.
		Oxygen, 48 parts	16		
		Hydrogen, 4 parts	32		Water, 36 parts ¹ .]

Observe that in this case the salt does not break up into ammonia and hydrogen nitrate, as we might perhaps expect from the way in which it was formed, but decomposes in a totally different way.

When a steady stream of bubbles has escaped for about a minute, you may place one of the large cylindrical jars over the hole in the shelf, and allow it to fill with gas. When full, remove it to another part of the shelf and bring another jar into its place. While this latter is filling, you may test the gas in the first jar. Slide it off the shelf with one hand, cover its mouth with a glass plate held in the other hand, raise it out of the trough and place it mouth upwards on the table. Remove the glass plate, and immediately introduce a cedar spill which has been lighted and *just* blown out, and shake it sideways in the jar, to quicken the glow. If it is rekindled, as in the case of oxygen, the gas is sufficiently pure; but it must be borne in mind that the end of the wood should be glowing rather brightly, in fact only just blown out; a mere spark is not enough to begin the combustion, as with oxygen. Proceed with the filling of the other jar and the bottles, carefully watching the decomposition of the salt, and not allowing it to go on too quickly.

When sufficient gas has been collected, take out the stopper of the retort, and set the latter aside to cool, still supported in the retort-stand.

¹ Or, in symbols,—



Properties of Nitrogen monoxide.

1. It is colourless, like the dioxide, but unlike the other oxides which you have prepared.

2. It is soluble in cold water, and has a sweetish smell and taste.

Pour into a small bottle of the gas about 50 c.c. of distilled water, and replace the stopper, inserting a small strip of thin paper between it and the neck of the bottle. Invert the bottle and shake it briskly for a few seconds, then hold it up to the light. Observe that bubbles of air are entering at the side of the stopper, thus showing that there has been an absorption of the gas. If the piece of paper had not been inserted at the side of the stopper, the latter would have become so firmly fixed in its place by the pressure of the external air, that it would have been difficult to loosen it. Shake the bottle again for a few seconds, then pour out some of the solution into a beaker and taste it. It will have acquired a sweetish taste and smell. Pour some of the solution into a test-tube and heat it over a lamp. As it gets hot, bubbles of the gas will be given off, proving that it is much less soluble in hot water than in cold water, as already mentioned.

3. It is much heavier than air, not combustible, and supports ordinary combustion well.

Put an empty cylindrical gas jar on the table, mouth upwards, and place in it the taper, lighted, leaning the wire against the side of the jar so that the taper may rest steadily at the bottom. Bring the mouth of one of the small bottles of gas close to the edge of the jar, withdraw the stopper, and gently pour the gas over the taper, precisely as if you were pouring out a liquid. The flame will become larger and more brilliant, but the gas will not itself ignite: thus proving nitrogen monoxide to belong to the same class as oxygen; *viz.* to be one of those gases which are not inflammable, but supporters of the combustion of a taper.

4. It gives up its oxygen readily.

Although nitrogen monoxide contains the smallest proportion of oxygen, yet it shows no decided tendency to combine with

more oxygen, like the dioxide; but, on the contrary, it gives up its oxygen more readily than any of the other nitrogen oxides (except the pentoxide).

(a) *Its decomposition by sulphur.*

Place the large bottle of gas on the table before you, and see that its stopper is sufficiently loose to be taken out when required. Put a small bit of sulphur into the deflagrating cup, heat it over the lamp until it enters into *full* combustion, then immerse it in the bottle.

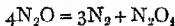
The sulphur will burn as brilliantly as in oxygen¹, but the blue flame will have a yellowish border. Sulphur dioxide (as shown by its odour and action on test-paper) will be formed, as in the experiment with oxygen (p. 122), thus proving that the gas you are dealing with contains oxygen. You will probably observe brown vapours in the bottle: these consist of one of the higher nitrogen oxides, the trioxide or tetroxide².

(b) *Its decomposition by hydrogen.*

Fill one of the larger gas jars with water and place it, inverted, on the shelf of the trough. Decant into it one measure of nitrogen monoxide, using the small thick jar as a measure. Add one measure of hydrogen (see note³) and mix the gases

¹ The sulphur must be heated considerably above its melting-point, and must be in full combustion in the air; otherwise it is extinguished when plunged into the gas.

² The probable explanation of their formation is that, owing to the intense heat, the oxygen of one portion of the gas oxidises another portion, thus,—



(Compare the decomposition of hypochlorites when heated, as explained under CHLORATES.)

³ A sufficient quantity of hydrogen for the above, and other similar experiments, may be made in the following way. Take a small gas jar; place in it two or three bits of granulated zinc, and fill it completely with dilute hydrogen sulphate (1 measure of acid to 6 of water). When a brisk action has commenced, place an inverted porcelain dish, or common saucer, about 8 cm. in diameter, over the jar like a cap; then, keeping the dish pressed close to the mouth of the jar, invert the apparatus quickly. The zinc will fall to the lowest part of the jar, and the evolved hydrogen will gradually fill the jar, displacing the acid, which collects in the dish and prevents the entrance of air. A minute bubble of air may possibly enter at the moment that the jar is inverted, if the operation is not skilfully performed, but so small a quantity will not materially vitiate the purity of the gas. When the jar is full of gas, fill up the dish with water, and raise the jar a little so that the remainder

by shaking the jar laterally. Decant some of this mixture into the small jar, close its mouth with a glass plate, place it on the table (mouth upwards), and apply a light to the mixed gases. The detonation which takes place is as violent as when the combination of hydrogen with free oxygen was effected in a similar way.

In this reaction it is found that the hydrogen only combines with the oxygen of the nitrogen monoxide, and that a quantity of nitrogen remains, equal in volume to the gas originally taken¹. Now, it has been proved (p. 131) that 1 measure of hydrogen combines with half a measure of oxygen: hence 1 measure of nitrogen monoxide yields 1 measure of nitrogen and half a measure of oxygen.

5. It can be breathed for a short time, but soon produces insensibility.

The most remarkable property of this gas, its property of producing a peculiar intoxication (whence its name of 'laughing gas') and finally insensibility when respired, is one which the student is advised not to try by himself; since particular precautions are necessary to obtain a perfectly pure gas for the purpose, and the effects of inhaling it vary with different individuals, and to some are decidedly injurious.

6. It has no action on nitrogen dioxide.

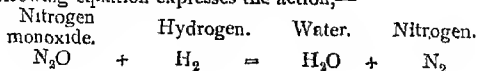
We have seen that nitrogen monoxide in many respects resembles oxygen: it may, however, be readily distinguished from the latter gas by the fact that nitrogen dioxide forms no orange vapours when mixed with it. The action of the two gases may be compared as follows.

Place two cylindrical gas jars, filled with water, on the shelf of the trough: decant into one some oxygen, into the other

of the zinc may fall into the dish; then close the mouth of the jar with a glass plate, and transfer it to the pneumatic trough.

This was probably the earliest method devised for the collection of a gas in order to examine its properties.

¹ The following equation expresses the action,—



some nitrogen-monoxide; then pass up into each a few bubbles of nitrogen dioxide (from the bottle reserved in the last exercise). Orange vapours will be formed in the jar containing oxygen, while no change will be observed in the other jar: nitrogen dioxide not having the power of decomposing nitrogen monoxide, although it will combine with free oxygen.

The series of nitrogen oxides which has just been examined affords excellent illustrations of the laws of chemical combination by weight and volume; and the student is recommended at this point to gain a knowledge of these laws, and also of the atomic theory and the system of chemical symbols. A short account of these is given in Appendix D, but a general textbook should, of course, be consulted as well.

11. CARBON.

[Symbol of atom, C

Weight „ 12 hydrogen-atoms.]

[In future, lists of the apparatus required will only be given where a more or less elaborate apparatus has to be set up, as for distillation, or the preparation and collection of a gas.]

The only one of the three allotropic forms in which carbon occurs, *viz.* diamond, graphite, and charcoal, on which experiments can be readily made is the last-named, charcoal. It is obtained by heating various organic substances (i. e. substances derivable from plants and animals), which all contain more or less carbon: for example, wood, bones, and oil or turpentine. When any of these substances are heated out of contact with air, a good deal of their carbon is separated in the form of charcoal.

Formation of wood charcoal.

Place a little sawdust, or a few splinters of wood (a couple of matches cut up into small pieces, the end coated with phosphorus being, of course, rejected) in a small test-tube, and heat the tube rather strongly, supporting it horizontally in a Bunsen's

holder, lest the condensed water should run down to the hot part and crack the tube. The wood will become black or 'charred' owing to the separation of carbon, while gases and vapours (such as wood naphtha) will be given off which will catch fire if a lighted match is held at the mouth of the tube. Drops of a liquid will also condense in the tube, which will redden blue litmus-paper; they consist mainly of water and hydrogen acetate ('wood vinegar'). You have thus analysed wood so far as to prove that it contains carbon, and also hydrogen and oxygen (since water is formed).

Formation of animal charcoal ('bone-black').

Put some pieces of bone into a ladle, cover them completely with sand (to prevent access of air, which would burn the carbon), and heat the whole to redness for about a quarter of an hour in an ordinary fire, while other experiments are proceeded with. Allow it to cool and then take out the charred pieces of bone, and grind them to fine powder in a mortar. This 'animal charcoal,' owing to its porosity and finely-divided state, has a strong power of absorbing some colouring matters and also many of the gases, as the following experiments will show¹.

(a) Its combination with colouring matter.

Put a little water into a test-tube, and add to it a drop of solution of indigo sulphate. Add to this some bone-black, shake the whole well together and heat it to boiling: then filter it into a clean test-tube, passing it again through the same filter if it does not run through clear. The filtrate will be nearly or quite colourless, the charcoal having absorbed the colouring matter of the indigo. From this property bone-black is much used in sugar-manufactories to render brown sugar white.

(b) Its power of absorbing gases.

Put about 2 c.c. of solution of hydrogen sulphide into a test-tube, add to it some bone-black, and shake the mixture

¹ Animal charcoal as purchased at the shops, which has been recently ignited in a covered porcelain crucible, may be used in this and the following experiment, and will be found to act even more powerfully than the charcoal prepared as above directed.

thoroughly for half a minute. You will find that the liquid has now lost all the offensive smell of the gas, which has been absorbed by the charcoal. The value of charcoal as a disinfectant is mainly due to this property of absorbing gases.

Formation of lamp-black.

Pour a few drops of turpentine into a small evaporating dish, and put into it a small tuft of tow to serve as a wick. Set fire to the turpentine and lower into the flame a white china plate, bottom upwards, depressing it so far as to admit only a very limited supply of air for the combustion of the turpentine. Under these circumstances the turpentine (which is a compound of carbon and hydrogen) will not be completely burnt, and a quantity of finely-divided carbon (the ordinary lamp-black) will be deposited on the surface of the plate. Oxygen has less affinity for carbon than for hydrogen, and hence, while the whole of the latter combines with oxygen, forming water, a part only of the carbon is converted into carbon dioxide, the rest appearing in the elemental condition. Compare the account of the Bunsen's burner, p. 4.

Direct combination of oxygen with carbon.

Fill a large gas bottle with oxygen gas¹. Select a splinter of charcoal, about 2 cm. in length (charcoal made from the bark of a tree burns most brilliantly); lay it across the deflagrating cup, and confine it in its place by a piece of copper wire, about 6 or 8 cm. long, twisted round the stem of the cup and made to press upon the charcoal, as shown in fig. 80. Heat the projecting part of the charcoal until it glows, and then immerse it in the jar of gas. It will at once enter into brilliant combustion, as it combines with the oxygen to form carbon dioxide².



Fig. 80.

To prove the formation of carbon dioxide, take out the

¹ If a supply in a gas-holder is not at hand, sufficient gas for this experiment may be made in a tube-apparatus, such as that which is shown in fig. 86 (under IODIDES) for making hydrogen iodide, a mixture of 6 grms. of potassium chlorate and 2 grms. of manganese dioxide being placed in the test-tube, and the gas collected by displacement.

² $C_2 + 2O_2 = 2CO_2$

charcoal when the combustion is over, and pour into the bottle 8 or 10 c.c. of lime-water (from a test-tube and not direct from the bottle). This will, on being shaken up, become turbid; a result which, as has been already seen (p. 69), is a characteristic proof of the presence of carbon dioxide.

Action of carbon in reducing metals from their oxides.

This depends upon the affinity of carbon for oxygen, illustrated in the last experiment, and is the principle of many of the smelting processes employed on a large scale.

Take about as much lead protoxide (litharge) as will lie on the end of a spatula, and powder it in a mortar. Make a small cup-shaped cavity in a piece of charcoal as directed on p. 102, fill it with the powdered substance, and direct the blowpipe flame down upon it (the mouth blowpipe being used, as in Exercise 10, p. 95). The lead protoxide will soon melt and effervesce owing to an escape of gas, and finally nothing but a bright globule of metallic lead will be left on the charcoal.

The carbon has reduced the lead protoxide, combining with its oxygen to form carbon oxides, which escape, while the lead is left in the metallic state¹.

COMPOUNDS OF CARBON WITH OXYGEN.

12. CARBON DIOXIDE.

[Formula of molecule, CO_2

Weight ,, 44 hydrogen-atoms.]

Apparatus required.—Flask, fitted with cork and tube-funnel as in Ex. 2; elbow-tube, with branches 8 cm. in length; ditto, with branches respectively 8 cm. and 18 cm. in length; corks; cork-boilers; rat-tail file; retort-stand; wire-gauze; wooden blocks; card; one gas bottle, holding 700 c.c.; four ditto, holding 200 c.c.; gas jar, 20 x 5 cm.; glass disc; test-tubes; small porcelain dish; Bunsen's burner; taper on wire; deflagrating cup.

Marble; strong common hydrogen chloride; solution of calcium hydrate (lime-water); solution of litmus; magnesium ribbon.

Preparation of carbon dioxide.

This gas can, as has been seen, p. 185, be formed by direct

¹ $4\text{PbO} + \text{C}_2 = 4\text{Pb} + 2\text{CO}_2$

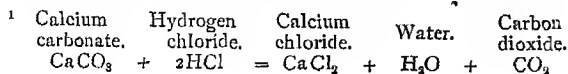
synthesis of carbon and oxygen; but it is usually prepared by an analytical process, i.e. by the decomposition of marble or chalk (calcium carbonate) by hydrogen chloride.

To illustrate this, put a fragment of marble into a small test-tube, and pour upon it 2 or 3 c.c. of dilute hydrogen chloride. An effervescence will at once begin, carbon dioxide being given off, while the marble gradually disappears. The exact nature of the action will be seen from the equation given below¹, which shows that the calcium of the marble combines with the chlorine of the hydrogen chloride, while some of the oxygen combines with the hydrogen of the acid, forming water, and the rest of the oxygen is evolved in combination with the carbon, as carbon dioxide.

[Hydrogen sulphate cannot be so conveniently used, since it forms a nearly insoluble compound with calcium, which covers the marble and hinders further action. Thus, if a few drops of dilute hydrogen sulphate are added to the mixture in the tube, a white precipitate of calcium sulphate appears, and the action soon ceases almost entirely.]

The gas, owing to its high density (about $1\frac{1}{2}$ times that of air), can readily be collected by downward displacement; the tube conveying the gas being led to the bottom of the bottle which is to be filled. This is preferable to collecting it over the pneumatic trough, since the gas is, as will be seen, rather soluble in water; although it may be collected over warm water, like nitrogen monoxide.

Fit up an apparatus as shown in fig. 81 (next page), the flask, cork, and tube-funnel being the same as used in preparing hydrogen; but another form of delivery tube is to be substituted for the bent tube then employed. It is made up of two elbow-tubes united by a cork joint; one of the elbow-tubes having two equal branches about 8 or 9 cm. in length, the other having one branch about 8 cm., the other about 18 cm. in length. The cork joint is made by boring a central hole through a small



cork (as free from fissures as possible), and pushing one branch of each tube into the hole until they meet in the middle of the cork. This forms an excellent joint, and has one special advantage over an india-rubber connector, *viz.* that it is stiff, and yet allows the tube to be turned round in any direction, retaining it in whatever position it is placed ¹.

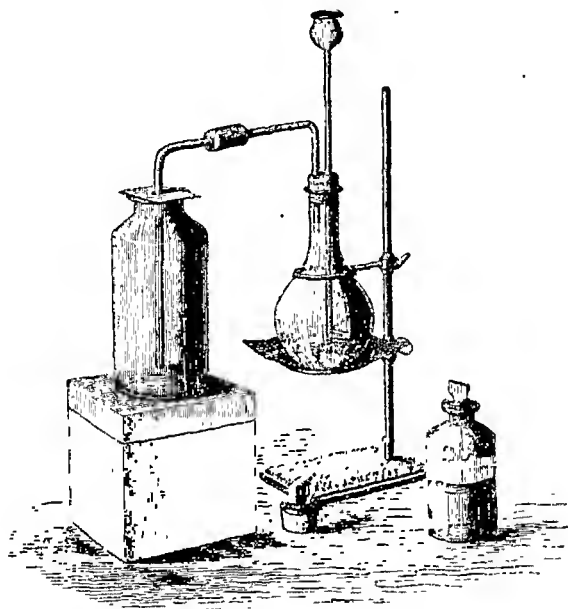


Fig. 81.

Place in the flask 20 grms. of marble, previously broken with a hammer into lumps rather larger than peas. Support the flask on the retort-stand at such a height that the open extremity of the delivery tube may be raised about 14 cm. above the table. Pass the end of the delivery tube into one of the bottles, supporting the latter on blocks, so that the tube may

¹ A similar but neater joint may be made by cutting off a piece of glass tubing about 3 cm. in length and 8 or 9 mm. in diameter internally, and (after fusing the sharp edges in the lamp) fitting into it the two elbow-tubes by means of rings of india-rubber tubing.

reach almost to the bottom. Over the mouth of the bottle lay a card in which a slit has been cut half-way across it (fig. 82), wide enough to admit the delivery tube. Pour through the funnel sufficient water to cover the marble, and then add, a few drops at a time, some strong common hydrogen chloride, until a brisk effervescence is set up, due to the evolution of carbon dioxide. After the lapse of half a minute, light the taper, remove the card from the mouth of the bottle, and pass the taper steadily down into it. It will probably be extinguished before it reaches the bottom, showing that the gas has partially filled the bottle. It may be withdrawn, relighted, and after a few seconds plunged again into the bottle, to ascertain the point to which the gas has now risen. When the flame is quickly and decidedly extinguished, just before it is actually within the mouth of the bottle, the latter may be considered to be full of gas. It should then be withdrawn, by first taking away the wooden blocks, then lowering the bottle slowly until clear of the delivery tube, and lastly inserting the stopper previously greased. Fill one large and three small gas bottles in this manner, more acid being added from time to time through the funnel. Reserve the large bottle for the last experiment, and examine the properties of the gas as follows:—



Fig. 82.

Properties of Carbon dioxide.

1. Its high density, and relation to ordinary combustion.

Take the cylindrical gas jar, and place in it the lighted taper, resting the wire against the side of the jar so as to support the taper steadily at the bottom. Bring the mouth of one of the small bottles of gas close to the edge of the jar, withdraw the stopper, and gently pour the gas over the taper, precisely as if you were pouring out a liquid¹. The taper will be immediately extinguished and the gas will not catch fire.

¹ Do not pour the gas directly over the centre of the jar, but at its edge, since the gas receives a forward as well as a downward impetus while the bottle is being inverted.

2. Its diffusion into other gases.

Carbon dioxide, although it has just been proved to be much heavier than air, will diffuse upwards into air, but the rate at which it does so is comparatively slow.

Place one of the small bottles of the gas on the table, and replace its stopper by a glass plate. Invert over it a similar, but empty, gas bottle; its stopper being removed and the mouths of the two bottles brought into contact. After the lapse of half a minute, remove the upper bottle, replace its stopper, pour into it a little lime-water, and shake it up. The cloudiness produced proves that carbon dioxide had really ascended, in spite of its great density, into the upper bottle.

[Fill the partially-emptied bottle again with gas, for other experiments.]

3. Its solubility in water.

Pour into a bottle of the gas sufficient distilled water to fill it one-third, and replace the stopper, inserting a small strip of thin paper between it and the neck of the bottle. Invert the bottle and shake it briskly for a few seconds; then hold it up to the light. Observe that bubbles of air are entering at the side of the stopper, thus showing that there has been an absorption of the gas. Shake the bottle again for a few seconds, then pour out a little of the solution into a beaker and taste it. The water will have acquired a distinct acid taste. Common 'soda-water' is simply a solution of this gas.

Pour some more of the solution into a test-tube, and heat it over a lamp. Bubbles of gas will be given off as the temperature rises, and if the liquid is boiled for a minute or two, the whole of the gas will escape.

4. Action of its solution in water on litmus.

Pour a few drops of solution of litmus into the solution of carbon dioxide obtained in the last experiment. It will be at once turned red, although the colour will not be so bright a red as that produced by the action of hydrogen nitrate (p. 160). It is probable that carbon dioxide (like sulphur dioxide, p. 122) forms a definite combination with water, hydrogen carbonate; but this has not been obtained in a pure condition, since it is easily decomposed

by heat. To prove this, pour some of the red liquid into an evaporating dish and boil it for a minute or two. Carbon dioxide will escape, and the blue colour of the litmus will be restored¹.

5. Its combination with metal-oxides or hydrates, to form carbonates.

*(a) Its action on calcium hydrate.

This has been alluded to already, p. 69, but will now be examined more fully.

(1) Fill a small test-tube about half full of lime-water, and pour the liquid into another bottle of the gas. Replace the stopper, inserting a slip of paper as in Experiment 3, and shake it slightly. The liquid will become milky, owing to the formation of ordinary calcium carbonate (the formula of the molecule of which is CaCO_3), of the same composition as chalk, which is insoluble in water.

(2) Now shake the bottle vigorously for several seconds at least. The turbid liquid will gradually become clear again, the precipitated calcium carbonate re-dissolving entirely.

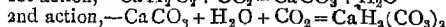
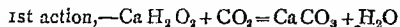
[If the liquid still remains turbid after repeated agitation, pour it into another bottle of gas, and agitate it again.]

The reason is that carbon dioxide can, when water is present, form another combination with calcium carbonate, called calcium-hydrogen carbonate, the formula of the molecule of which is $\text{CaH}_2(\text{CO}_3)_2$, and which is readily soluble in water². This latter action explains the presence of much of the calcium salts found in spring-water (as may have been proved already, p. 75).

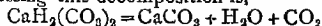
(3) If, now, some of the clear solution be poured into a test-tube and heated to boiling over a lamp, the calcium-hydrogen carbonate will be decomposed; carbon dioxide will be given off, and the insoluble calcium carbonate re-precipitated³.

¹ If the colour remains red, it shows that a little vapour of hydrogen chloride has passed over from the flask. To obtain a pure gas it should be passed through a wash-bottle (see fig. 83, p. 198) containing a little distilled water (in which hydrogen chloride is extremely soluble) before being collected.

² These two successive actions may be expressed by the following equations,—



³ The equation expressing this decomposition is,—



This experiment illustrates the cause of the hard crust of calcium carbonate formed in kettles and boilers in which 'hard' spring-water has been boiled. (See also under CALCIUM.)

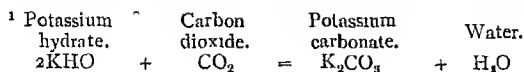
(b) *Its action on potassium hydrate (caustic potash).*

Put a small bit of solid potassium hydrate, about half the size of a pea, upon a watch-glass. Fill a small test-tube with carbon dioxide by displacement, withdrawing it from the delivery tube slowly, and closing its mouth at once with the thumb. Introduce into the tube 3 or 4 drops of water from the jet of the washing bottle, and then put in the fragment of potash, closing the mouth again tightly at once. Invert the tube, and shake it so as to moisten the sides with the solution of potassium hydrate which is rapidly formed. You will soon feel the thumb strongly pressed inwards, owing to the absorption of the gas. In about half a minute, place the mouth of the tube below the surface of some water in a jug or pan, and withdraw the thumb gradually. The water will rush in violently, and nearly or quite fill the tube, showing that the absorption of the carbon dioxide by potash has been rapid and complete. Hence a solution of potash can be effectively used to withdraw carbon dioxide from a mixture of gases (as will be seen in Exercise 14). The action is quite analogous to that on calcium hydrate, potassium carbonate being formed¹.

6. *Its decomposition by magnesium.*

Magnesium has so strong an affinity for oxygen, as has been proved already, p. 124, that it will do what a candle cannot do, *viz.* decompose carbon dioxide, combining with its oxygen and leaving its carbon.

Affix a piece of magnesium ribbon, about 16 cm. in length, to the flange of the deflagrating cup (the cup itself with its wire being removed) or to a cork, as directed in the case of the watch-spring, p. 123, so that its extremity may reach nearly to the bottom of the large bottle of carbon dioxide. Hold the end of the ribbon in the lamp-flame until it begins to burn with a



brilliant white light, then plunge it slowly into the bottle of gas. It will continue to burn brilliantly, forming white flakes of magnesium oxide interspersed with black particles which consist of carbon. In order to separate the latter, pour into the bottle, when the combustion is over, a little distilled water, shake it up and pour it, with the suspended particles, into an evaporating dish. Add eight or ten drops of strong hydrogen chloride, and heat the liquid over a lamp. The magnesium oxide will dissolve, while the thick flakes of carbon will remain floating undissolved in the clear liquid. This experiment proves that the gas which you are examining contains carbon, and also that some substances will burn in a gas in which a taper will not burn.

[That these black particles are really carbon may be readily proved by collecting them on a small filter, washing them with several changes of water (until the washings give no precipitate when tested with silver nitrate) and then drying them thoroughly, the filter being put in a porcelain dish on a sand-bath. When they are quite dry, detach some of them from the filter, and put them into a small dry test-tube. Put a cork *loosely* into the tube, and heat it rather strongly over a lamp. At a red heat the particles will glow as they combine with the oxygen of the air in the tube to form carbon dioxide. To prove that this gas is really formed, set aside the tube (still corked) in some sand to cool, and then pour into it a little lime-water, which will, on being shaken up, become cloudy.

Observe that, while in the last experiment you had a good example of chemical analysis, carbon dioxide being decomposed and one of its elements (carbon) separated in the free condition, in this experiment you have an equally good example of synthesis, the carbon combining directly with oxygen to form carbon dioxide.]

Additional Experiments.

7. Decomposition of carbon dioxide by zinc or iron.

When carbon dioxide is passed over strongly-heated zinc or iron, the metal takes out from it only one-half the oxygen it contains (and not the whole, as the magnesium did in the experiment last made), and carbon monoxide remains. This reaction is important as showing that the molecule of carbon dioxide contains at least two atoms of oxygen (since the quantity of oxygen in it can be divided

and taken out in two instalments), and it may be tried on a small scale as follows:—

Put a few small bits of zinc into the bulb of an ignition tube (which should be of rather thick, difficultly-fusible glass); add enough finely powdered chalk or marble to nearly fill the bulb, and shake the two substances together until thoroughly mixed. Heat the bulb strongly by a gas blowpipe, and when it is red-hot, hold a lighted match to the end of the tube. The gas given off will be found to burn with a blue flame, and cannot, therefore, be carbon dioxide.

What has happened is this—the calcium carbonate has been decomposed by the heat, carbon dioxide being given off. This has given up half its oxygen to the red-hot zinc, being thus reduced to carbon monoxide, which, as will be seen in Exercise 14, burns in air with a characteristic blue flame.

8. Its decomposition by plants in presence of light.

This action, which it is best to try on a bright, sunny day, supplies us with a direct proof that carbon dioxide contains oxygen, and also explains why it does not accumulate in the air, although it is being constantly produced by the processes of respiration and combustion (p. 144).

Fill a large gas bottle with common fresh water and pass into it some carbon dioxide from an apparatus fitted up in the usual way (fig. 81, p. 188)¹. When the gas has bubbled through the water for 8 or 10 minutes (not more), withdraw the elbow-tube and put into the water a bunch of freshly-gathered parsley or water-cress, or any vigorously growing leaves, taking care that no air-bubbles remain entangled among the leaves. Fill up the bottle to overflowing with water, place a large porcelain dish or a common plate over the mouth, and invert the bottle quickly, holding the plate firmly against its mouth so that no air may enter. Pour a little water into the dish to ensure the exclusion of air, and expose the whole to bright daylight (sunlight if possible) for 6 or 8 hours. Bubbles of gas will be observed to collect on the under side of the leaves, and rise to the top of the bottle. The growing plant has inhaled the carbon dioxide (as animals inhale oxygen) and has appropriated its carbon, while the oxygen is set free as gas. If, however, the bottle is kept in a dimly-lighted room, or if the day is

¹ Or some of the contents of a bottle of soda water (which is simply a strong solution of carbon dioxide) may be added to the water in the bottle. In any case there should not be very much carbon dioxide in the water.

very dull, only a slight action will take place; showing that light is required for the decomposition.

If 8 or 10 c.c. of gas are obtained, it may be proved to be oxygen by immersing the bottle in a deep pan, or the pneumatic trough, shaking it to detach all bubbles from the leaves, then decanting the gas into a test-tube (using a funnel as explained, p. 107), and testing it with a glowing match, which will be re-lighted.

13. CARBONATES.

	Formula of molecule.
[Typical examples,—Calcium carbonate,	CaCO_3
Sodium carbonate,	Na_2CO_3
Ammonium carbonate, $(\text{H}_4\text{N})_2\text{CO}_3$]	

These are salts which contain the carbonate radicle, a group consisting of 1 atom of carbon and 3 atoms of oxygen, represented by the formula CO_3 . They are usually formed by the action of carbon dioxide on metal-oxides or hydrates, as already illustrated in expt. 5, p. 192.

Properties of Carbonates.

***1. When mixed with hydrogen nitrate they are decomposed, giving off carbon dioxide.**

Put a small fragment of sodium carbonate (common 'washing-soda' will do) into a test-tube, and add 1 or 2 c.c. of dilute hydrogen nitrate. Effervescence will take place, and the gas given off may be proved to be carbon dioxide in the following way:—

Dip the end of a pipette into lime-water, and withdraw it without closing the upper end of the tube with the finger, so that a drop of lime-water is retained in the narrow jet by capillary attraction only. Introduce the pipette into the test-tube containing the gas, and lower it until the jet is about 1 or 2 cm. above the liquid at the bottom of the test-tube. While it is in this position suck a very little of the gas through the lime-water¹; then withdraw the pipette and hold it up to the light, or, better, against some dark background as the sleeve of the coat. The drop of lime-water, as it subsides again into the jet of the pipette, will be seen to be turbid¹.

¹ A drop of lime-water at the end of a glass rod will show turbidity in

[Another method of applying this test, which may sometimes be useful, is the following :—

Take the cork fitted with tubes out of the washing-bottle (fig. 17, p. 11), and adapt it (the tubes still remaining in it) to a test-tube large enough to fit it¹, adjusting the long branch of the jet-tube so that it may reach nearly to the bottom of the test-tube. Put 4 or 5 c.c. of lime-water into the test-tube, then fit the cork again into its place, and insert the jet of the tube into the test-tube containing carbon dioxide. Apply your mouth to the other tube and suck a little of the gas through the lime-water, which will become turbid.]

[The tubes and cork should, of course, be rinsed with distilled water before being replaced in the washing bottle.]

A similar experiment should be tried with at least one other carbonate, such as chalk, oolite, egg-shell, or ammonium carbonate (smelling salts). It will be found that in every case carbon dioxide will be given off.

It will be instructive also to try the effect of dilute hydrogen nitrate upon substances which resemble marble in appearance, such as alabaster, and which resemble chalk, such as plaster of Paris. No gas will be given off from these substances; and thus we learn a very useful method of discriminating between various classes of minerals, resembling each other in structure and appearance but differing in chemical composition. Slate, for instance, and basalt may be easily distinguished from black marble and limestones which resemble them; the latter causing an effervescence when a drop of acid is put on them, the former causing none.

***2. They have, when dissolved in water, an alkaline reaction.**

Prove this by putting a drop of solution of sodium carbonate or ammonium carbonate, taken up with a glass rod, upon strips of reddened litmus and turmeric paper laid on a white plate.

the same way, when lowered carefully and steadily into the test-tube. In either way very small traces of carbon dioxide may be detected.

¹ If you have no test-tube of the proper size, a cork may be fitted to a test-tube and holes bored in it to receive the tubes of the washing bottle as above; or ordinary elbow-tubes may be used, as in fig. 75, p. 145.

14. CARBON MONOXIDE.

[Formula of molecule, CO

Weight " 28 hydrogen-atoms.]

Apparatus required.—Pneumatic trough; flask, with elbow-tubes and tube funnel, used in Exercise 12; wide-mouthed bottle holding about 150 or 200 c.c. (No. 34, p. 10); corks; cork-borers; rat-tail file; bent delivery tube used in Ex. 1; wooden blocks; retort-stand; wire gauze; argand burner; india-rubber connector; two jars, 20 x 5 cm.; one ditto, 10 x 3 cm.; three small gas bottles; glass disc; taper on wire.

Crystallised hydrogen oxalate; strong common hydrogen sulphate; solution of sodium hydrate or potassium hydrate (caustic soda or potash) containing 20 grms. of the substance dissolved in 100 c.c. of water; solution of calcium hydrate (lime-water); solution of litmus; small bottle of oxygen.

Preparation of Carbon monoxide.

One reaction in which this gas is formed has been already tried, p. 193; it is, however, usually prepared by the decomposition of hydrogen oxalate (oxalic acid). This substance contains the elements of water, carbon dioxide, and carbon monoxide, as may be seen by the formula of its molecule, $\text{H}_2\text{C}_2\text{O}_4$ (which $= \text{H}_2\text{O} + \text{CO}_2 + \text{CO}$). When it is heated with strong hydrogen sulphate, the latter combines with the elements of water, and the two carbon oxides are liberated in a state of mixture¹. The carbon dioxide may be withdrawn by allowing the mixed gases to pass through a solution of potassium hydrate, which (as has been seen, p. 192) unites readily with carbon dioxide, but has, under ordinary conditions, no action on carbon monoxide. A bottle containing this solution must therefore be interposed between the generating flask and the pneumatic trough.

Adapt a cork to a bottle with a rather wide mouth, of about 150 c.c. capacity. Bore two holes in the cork: into the one fit the bent delivery tube used in the preparation of hydrogen; into the other fit the longer branch of the elbow-tube used in Exercise 12, passing the tube through the cork to such a distance that its extremity may reach almost to the bottom of

¹ Hydrogen oxalate. Hydrogen sulphate. Dilute hyd. sulphate. Carbon dioxide. Carbon monoxide.
 $\text{H}_2\text{C}_2\text{O}_4 + \text{H}_2\text{SO}_4 = \text{H}_2\text{O}, \text{H}_2\text{SO}_4 + \text{CO}_2 + \text{CO}$

the bottle. Before the cork is finally fitted into its place, fill the bottle to about three-fourths of its height with a solution of caustic potash or soda, made by dissolving 20 grms. of the substance in 100 c.c. of water. Support it on blocks at such a height that the delivery tube may dip under the shelf of the pneumatic trough. In the next place, take the flask, fitted with the short elbow-tube and funnel, used in Exercise 12, place in it 20 grms. of crystallised hydrogen oxalate, and fix it in the

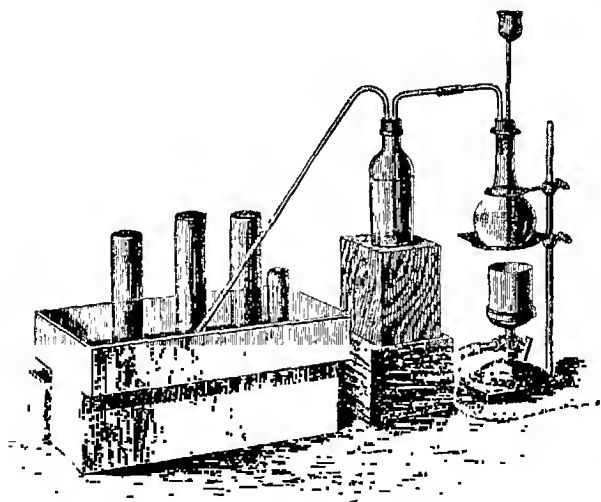


Fig. 83.

retort stand, with a piece of wire-gauze under its bottom, at such a height as to admit of the argand burner being placed under it, and to allow the elbow-tube to be connected with the tube of the wash-bottle by a short piece of india-rubber tubing.

The whole apparatus will then appear as above, fig. 83. †

Pour into the flask about 60 c.c. of strong common hydrogen sulphate. As there are several chances of leakage, it will be necessary to test the joints as directed on p. 126, and not to proceed with the experiment until they are all made tight. The flask may then be gradually heated with the lamp, especial

care being taken to avoid any chance of cracking it, and thus spilling the strong acid to the damage of table, clothes, and hands. While the flask is being heated, the jars and three small gas bottles may be filled with water and inverted on the shelf of the trough.

When the mixture in the flask begins to effervesce, the heat should be moderated, so that the stream of gas may pass through the solution in the wash-bottle in bubbles not succeeding each other too quickly to be counted.

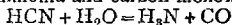
After a sufficient quantity (about two jars full) of the gas has been rejected, the jars and bottles may be filled for experiments. As soon as this is done, the india-rubber connector between the flask and the wash-bottle should be taken off, and the flask removed at once into a draught cupboard or the open air, as the gas is poisonous and should not unnecessarily be allowed to escape into the room.

[The best method of procuring carbon monoxide is undoubted that which was discovered by Fownes, depending on the decomposition of potassium ferrocyanide when heated with hydrogen sulphate¹.

The apparatus may be the same as that described above. The wash-bottle, although not absolutely necessary, is useful to absorb traces of hydrogen cyanide and sulphite, and carbon dioxide, which come over.

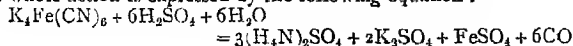
Place in the flask about 80 c.c. of strong hydrogen sulphate. Weigh out 15 grms. of potassium ferrocyanide, reduce the salt to powder, and add it little by little to the acid in the flask, shaking between each addition, in order to prevent the salt caking into lumps. Add also about a teaspoonful of fine dry sand, to promote the regular evolution of gas. Now fit in the cork and proceed to heat the mixture, watching carefully for the first evolution of gas.

¹ The reaction is rather complicated, but the principle of it is this:—Hydrogen cyanide is first formed by the action of the acid upon the potassium ferrocyanide; and this acts upon the water present (as water of crystallisation) to form ammonia and carbon monoxide. Thus—



The ammonia combines with the excess of hydrogen sulphate, forming ammonium sulphate, and the carbon monoxide is given off.

The whole action is expressed by the following equation:—



No gas comes off until the temperature is pretty high, and then there is a sudden rush, which must be moderated by withdrawing the lamp at once. The temperature should not be allowed to rise higher than is necessary to obtain a slow stream of the gas. It is better not to pour water into the flask for the purpose of washing out the residue, until as much of the latter as possible has been shaken out; otherwise the sudden heat produced by the addition of water to the strong acid is likely to crack the flask.]

The following properties of the gas should now be examined, and the many points of contrast between the two carbon oxides should be carefully noted.

Properties of Carbon monoxide.

1. Its insolubility in water, and neutral action on litmus.

Pour some water into a bottle of the gas, put a slip of paper between the neck and the stopper, invert the bottle, and shake it. No entrance of air in bubbles will be observed. Pour a few drops of solution of litmus into the water in the bottle: there will be no change of colour¹.

*2. Its relation to combustion.

Plunge a lighted taper into a jar of the gas, placed mouth upwards on the table. The taper will be extinguished, and the gas will burn with a characteristic blue flame. In burning it unites with the oxygen of the air to form carbon dioxide, as will be presently proved.

3. Its direct union with oxygen.

Decant into one of the gas jars two measures of carbon monoxide (the measure being the small gas jar). Add one measure of oxygen, transfer the jar to the table, and apply a light. The gases will unite with a slight explosion, forming carbon dioxide², as proved in the next experiment.

4. Its inability to act on calcium hydrate.

To try this satisfactorily, all traces of carbon dioxide must first be got rid of. For this purpose, pour into a bottle of

¹ If the gas has been insufficiently washed, the colour of the litmus may be slightly changed owing to the carbon dioxide present.

² $2\text{CO} + \text{O}_2 = 2\text{CO}_2$.

the gas about .10 c.c. of solution of potassium hydrate, and shake it up thoroughly for half a minute; then decant some of the purified gas into the small gas jar, filling it completely, and place it, covered with a glass plate, on the table. Pour into it quickly a little lime-water (remembering that carbon monoxide is rather lighter than air, and hence the cover should not be removed more than necessary) and shake it up. No considerable turbidity should be produced ¹.

[Otherwise the gas is not pure and must be again shaken up with potash, and another portion decanted and tested in the same way.]

Now apply a light to the gas and allow it to burn in the jar. Replace the glass plate as soon as the combustion is over, and shake up the lime-water in the gas. It will now become very turbid, proving that carbon dioxide has been produced in the combustion.

COMPOUNDS OF CARBON WITH HYDROGEN.

These are very numerous; turpentine, benzol, paraffin oil, paraffin wax, ethylene ('olefiant gas'), and methane ('marsh gas'), being the commonest examples.

15. ETHYLENE (Olefiant Gas).

[Formula of molecule, H_4C_2

Weight „ 28 hydrogen-atoms.]

Apparatus required—Pneumatic trough; flask, fitted with delivery tube and funnel, used in Ex. 2; beaker; glass measure; one small and two large gas jars; three small gas bottles; taper on wire; glass disc; elbow-tube; india-rubber connector.

Alcohol (methylated spirits will do); strong common hydrogen sulphate; solution of calcium hydrate; bottle of chlorine; bottle of oxygen.

• Preparation of Ethylene.

This gas is obtained in a pure condition by heating a mixture of alcohol and hydrogen sulphate. The simplest (although

¹ It must be remembered that common water usually gives a cloudiness when mixed with lime-water (p. 75), and a slight action of this kind due to the water used in the trough must be allowed for.

probably not a complete) view of the action is, to regard alcohol as containing the elements of ethylene and water; the latter combines with the hydrogen sulphate, while ethylene is liberated¹.

Measure 25 c.c. of common alcohol (methylated spirits will do) into a beaker capable of holding at least 150 c.c. Place the vessel in a basin of cold water, or hold it in the pneumatic trough, and add to it, slowly at first, 60 c.c. of strong hydrogen sulphate. The mixture will grow dark, and probably boil at first, showing that chemical combination is going on between the alcohol and the acid, and the temperature should be kept down as much as possible by agitating the flask in the surrounding water and adding the acid slowly. While the liquid is cooling you may arrange an apparatus similar to that used for preparing hydrogen, fig. 72, p. 126, putting about a teaspoonful of sand in the flask in order to lessen the tendency of the liquid to froth up². Pour the mixture of acid and alcohol into the flask, shake it until thoroughly mixed with the sand, and heat it cautiously to the boiling point (about 150°); being careful so to regulate the heat that the contents of the flask may not froth over into the delivery tube. Reject the two first jars full of the gas, and then proceed to fill three jars and two small gas bottles, for examination of the properties of the gas.

[When the jars &c. are filled, lower the lamp-flame considerably, but leave the apparatus in its place; since more gas will be wanted for expt. 3 *b*.]

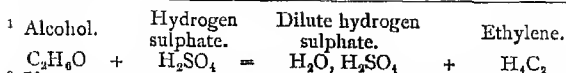
Properties of Ethylene.

1. Its peculiar fragrant odour will have been already noticed.

2. Its insolubility in water is proved by the fact that it can be collected without loss over the pneumatic trough.

3. Its union with oxygen.

(a) Place a jar of the gas mouth upwards on the table, and



² If a very pure gas is required a wash-bottle containing caustic soda must be interposed between the flask and the delivery tube, as in preparing carbon monoxide, fig. 83, p. 198, in order to retain any sulphur dioxide and carbon dioxide which may come over.

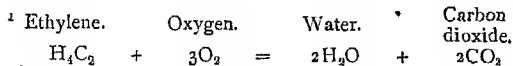
plunge a lighted taper into it. The taper will be extinguished, but the gas will burn with a bright white flame. By pouring some water from a jug into the jar, the gas will be forced out, and the flame seen to better effect.

(b) Attach to the end of the delivery tube an elbow-tube, as in experiments with hydrogen, fig. 74, p. 132 (omitting the jet), and heat the mixture in the flask until more gas is evolved. Test carefully the purity of the gas by filling a test-tube with it, as directed, p. 133; and when you are satisfied that the gas is pure, light it at the end of the tube. Hold over the flame (for a few seconds only) a small empty gas bottle and observe that moisture is deposited in it. Pour a little lime-water into the bottle, and shake it up; it will become cloudy. You have thus proved that water and carbon dioxide are produced during the combustion of ethylene, and therefore that the gas must contain hydrogen and carbon.

Depress a porcelain dish or white plate into the flame; it will at once be covered with a dense black soot. The reason of this will be clear from what has been learnt already respecting the principle of the Bunsen's burner (p. 4) and the blowpipe flame (p. 98). The gas issuing from the jet cannot at once obtain sufficient oxygen to combine with all the carbon and all the hydrogen which it contains; hence some of the carbon, having less affinity for oxygen than hydrogen has, is separated and heated white-hot in the flame, imparting to the latter all its brilliant whiteness. This carbon is cooled down and deposited upon the surface of the porcelain.

[The flask may now be set aside, to be washed out when the mixture is quite cold (not before, since it is not safe to add water to hot sulphuric acid).]

(c) Since it can be proved that nothing but water and carbon dioxide are formed by the action of oxygen upon ethylene, it is easy to construct an equation expressing the change¹, and to



The formulæ represent single molecules of the substances, and the figures

calculate from it the volume of oxygen required to combine with a given volume of ethylene. We thus find that three measures of oxygen are required for a single measure of ethylene.

Fill one of the larger gas jars with water, and decant into it one measure of ethylene and three measures of oxygen gas, using the small strong jar as the measure. Decant some of the mixture into the small jar, and apply a light to it. The gases will unite with an explosion which is even more violent than that produced by the union of oxygen and hydrogen under the same conditions; and the experiment should only be made with small quantities of the gases in a thick jar. After the experiment, allow the remainder of the mixed gases to escape into the air, to avoid any chance of an accident.

[If no chlorine is at hand, the two following experiments may be deferred until the exercise on CHLORINE, a small bottle of ethylene being reserved for the purpose.]

4. Its direct union with chlorine.

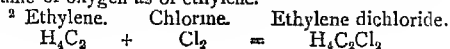
Decant into a gas jar one measure of ethylene, and add an equal volume of chlorine; then leave the mixture on the shelf of the trough in a good light for a minute or two. Combination will readily take place, one molecule of ethylene uniting with one molecule of chlorine to form ethylene dichloride², a liquid which collects in oil-like drops on the sides of the jar and on the water as the latter rises in the jar.

It was owing to the oily appearance of this liquid that ethylene originally received the name of 'olefiant' gas.

5. Its decomposition by chlorine.

At ordinary temperatures chlorine simply unites directly with ethylene, as above shown. But at high temperatures its action

on the left hand of the formulæ express the number of molecules of the substance which take part in the action. Now it is pretty certain that equal volumes of gases, whatever their chemical nature, contain the same number of molecules; therefore if we have to take three times as many molecules of oxygen as of ethylene, we must measure out three times as large a volume of oxygen as of ethylene.



is entirely different: its affinity for hydrogen is so great that it decomposes the gas, uniting with the hydrogen and leaving the carbon wholly uncombined¹.

Decant into a gas jar two measures of chlorine and add one measure of ethylene: then, without delay, cover the mouth with a glass plate, place the jar on the table mouth upwards, and apply a light. The action will be quick but not explosive, accompanied by a reddish flame, and formation of a dense cloud of soot, consisting of the unconsumed carbon.

It will be seen that the action is very analogous to that of oxygen already noticed in expt. 3 *b*, but in this case the whole of the carbon remains unacted on.

Additional Experiments.

Formation of Coal Gas.

Ethylene is present in ordinary coal gas to the extent of about 5 measures in 100, and is the chief cause of the brilliancy of a gas flame.

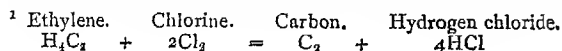
Coal contains carbon, hydrogen, oxygen, and nitrogen; and when it is decomposed by a strong heat some of the carbon and hydrogen combine to form ethylene. Many other gases are produced at the same time, such as methane (another hydro-carbon), hydrogen, carbon monoxide, and carbon dioxide (this last being separated as far as possible by means of lime); also water which contains ammonium compounds, and the very complex mixture called 'coal-tar'; while a good deal of the carbon remains behind in the form of 'coke.'

The decomposition of coal may be tried on a small scale as follows:—

Powder a little coal very finely, and half fill the bulb of an ignition tube with it.

[To do this quickly, scrape up some of the powder in the mortar with the open end of the tube, then tap the tube (held vertically, bulb lowermost) against the side of the mortar, so as to shake the powder down into the bulb; then scrape up a little more of the powder, and shake it down in a similar way; and so on, until the bulb contains enough.]

Attach a glass jet to the ignition tube by an india-rubber con-



nector, and support it horizontally in a Bunsen's holder; then heat the bulb pretty strongly. Water and a black, tarry liquid will condense in the tube, and gases will come off which burn with an intensely white flame when a lighted match is held to the jet.

The water may be afterwards tested with reddened litmus, when the presence of ammonium compounds will be shown by their alkaline reaction. Nearly all the ammonia of commerce is (as already mentioned, p. 147) obtained from this 'gas liquor.'

Properties of Coal Gas.

1. It is much lighter than air (its density being about 0.4).

This has been proved already in collecting it by upward displacement, p. 108. It may be farther shown by attaching an elbow-tube to the gas supply by an india-rubber tube, dipping the end of it into some solution of soap (p. 135) and blowing a bubble with the gas, which will quickly rise. This illustrates the use of coal gas for filling balloons.

2. It combines readily with oxygen, when heated.

Fill one of the larger cylindrical jars with water, and decant into it one measure of coal gas (from an india-rubber tube connected with the gas supply), and one measure of oxygen, the small cylindrical jar being used as the measure. After shaking the jar to mix the gases, decant some of the mixture into the small jar and apply a lighted taper to its mouth, when a sharp explosion will take place. This shows the danger of bringing a lighted candle into a room into which some gas has accidentally escaped.

3. Its heating and lighting powers.

Both of these are due, more or less directly, to the strong affinity between the gases of which it is chiefly composed and oxygen. The heat produced by its combustion has been illustrated in the account of the Bunsen burner, p. 5. The reason of the light it gives will be plain from what has been said respecting ethylene, p. 203, and will be further alluded to in the next Exercise.

16. COMBUSTION AND FLAME.

In many previous experiments substances will have been noticed to undergo 'combustion,' or to 'burn,' as it is called. Thus when iodine and phosphorus were placed in contact (p. 81), the whole caught fire. When sulphur and copper were

heated together (p. 82), the mixture glowed brightly. When sulphur was heated alone in air it caught fire, and burned brightly when put into oxygen (p. 122), as did steel (p. 123) and charcoal (p. 185) under like circumstances. Again, you have found several gases to be readily inflammable, such as hydrogen (p. 129), carbon monoxide (p. 200), and ethylene (p. 202); burning in air with characteristic flames. We may now consider more minutely the general meaning of the common terms 'combustion' and 'burning.'

Take a bit of magnesium ribbon about 10 or 12 cm. long, and, holding it by one end in a pair of crucible tongs, bring the other end into the flame of a Bunsen burner until it catches fire; then hold it over an iron dish, such as the sandbath, until the combustion is over. Observe the intense bluish white light and the clouds of white smoke produced during the burning, and the white residue or 'ash' which drops into the iron dish.

It was formerly thought that in this and similar cases, such as the burning of a candle, something was lost by the substance (indeed, the matter of the candle was believed to be annihilated entirely). But if all the white substance, smoke and ash, produced in the burning of the magnesium is collected and weighed¹, it is found to weigh more than the original piece of metal, and to consist of oxygen combined with magnesium. Similarly when a candle 'burns away,' the carbon and hydrogen of which it is mainly composed are found not to be destroyed but simply to form with the oxygen of the air compounds (7/12.

¹ A larger and more sensitive balance than the one described in the list of apparatus is required to do this satisfactorily. If such a balance is at hand, the increase in weight may be shown as follows. Take a piece of fine iron wire-gauze about 12 cm. square, and turn down its four corners so as to support it about 2 cm. above the table. Cut off a piece of magnesium ribbon about 30 cm. long, coil it into a loose spiral, leaving one end slightly projecting, and lay it upon the gauze. Place over it a rather large, light beaker, about 15 x 9 cm., put the whole upon a scale of the balance, and weigh it carefully. Then place it upon a plate, take off the beaker and light the magnesium by holding a Bunsen burner flame to the projecting end, replacing the beaker as soon as the metal begins to burn. Thus the greater part of the product of combustion will be retained in the beaker and on the wire-gauze. When the whole of the apparatus is quite cold (not before), replace it on the scale; notice the increase in weight and determine its amount.

carbon dioxide and water, as has been proved already, p. 144) which happen to be invisible, and so were formerly ignored. It is easy to prove by means of a good balance that these products weigh more than the original candle by the weight of the oxygen with which they have combined.

Again, it was formerly thought that oxygen was necessary for combustion. But in two of the above-named instances, *viz.* the combustion of phosphorus with iodine, and of copper with sulphur, and also in an experiment lately made (p. 204) on the combustion of ethylene with chlorine, all the usual phenomena of combustion were observed although no oxygen took part in the action.

The one fact common to all the above examples of combustion is, that *chemical combination is taking place*: and thus we arrive at the following general definition of combustion, *viz.* that it is the combination of substances chemically with evolution of heat, which in most cases is so intense as to cause light.

Next, with regard to the nature of Flame. It will have been noticed, that in *some* only, not all, of the above cases flame accompanied the chemical action. If we endeavour to discover some condition which is present in all cases where flame is observed, and absent in all cases where flame is absent, we shall see that whenever the substances concerned are either gases (such as hydrogen and oxygen, chlorine and ethylene) or easily volatile (such as phosphorus and iodine) flame occurs in their combustion; while when they are, or one of them at any rate is, a difficultly-volatile solid (as in the case of copper and sulphur, charcoal and oxygen) no flame but only a bright glow is noticed. Thus we learn that flame is a phenomenon occurring in the combustion of gases or vapours only, being, in fact, simply glowing gas.

Experiments on Flame.

1. Structure of a candle- or gas-flame.

This has been described already (p. 97). You have there been told that such a flame is, under ordinary conditions, hollow; the innermost portion not being really flame at all, but simply

unburnt gases or vapours. This you may now prove in several ways.

1. Light the Bunsen burner, closing the air-holes so that the gas burns with the usual luminous flame. Hold a piece of platinum foil vertically edgeways in the flame, with its lowest edge touching the top of the burner. Notice that the part of the foil which is in the middle of the flame is not even heated to redness, while the portions just outside this glow brightly; showing, in fact, a vertical section of the true flame.

2. Light a candle, protecting the flame if necessary from draughts of air. Hold half a sheet of writing-paper horizontally over the flame, and without delay bring it quickly down flat upon the flame until it nearly touches the wick. As soon as it shows signs of scorching on the upper surface, remove it quickly from the flame, and notice that soot has been deposited on the under surface, principally in the form of a hollow ring, and not in a uniform patch, as would have been the case if the flame had been the same in structure throughout.

3. Take a bit of glass tubing about 3 or 4 mm. in internal diameter (not more) and 13 or 14 cm. long; hold it slanting in a Bunsen holder (like the test-tube in fig. 62, p. 77) and bring its lower end into the middle of the gas flame, *just above* the upper end of the pipe. The unburnt gas will thus be conveyed away, and can be kindled by applying a light to the upper end of the tube.

[The same experiment may be made with a candle-flame; but the tube should be slightly heated before bringing it into the flame close above the wick, otherwise the wax-vapour is liable to condense before it reaches the upper end of the tube where it is to be burnt.]

4. Depress a piece of fine wire-gauze about 12 cm. square (not less) upon the gas-flame, or the candle-flame, in the same way as the paper in expt. 2. The wire-gauze will cut off the flame as completely as if it was a solid plate of metal and not a sieve; and a good horizontal section of the flame can be seen by looking down on it from above.

Action of Wire-gauze on Flame.

You have just observed wire-gauze to possess the property of cutting off a flame completely. This depends on the fact that metals are very good conductors of heat. In order that combustion may go on, i.e. that chemical combination may take place, a rather high temperature is required in the case of coal-gas or wax-vapour and oxygen. Now the wire-gauze, when introduced into the flame, conducts away the heat so quickly that the gases are cooled down below the temperature at which they can combine; and thus the flame ceases to exist, and the gas and air pass through the meshes of the gauze simply mixed. The following experiments will further illustrate this property of wire-gauze (which has received an important application in the Davy safety-lamp, used in coal mines).

1. Depress the piece of wire-gauze on the flame as in the last experiment, and hold a lighted match close above it. The mixture of gas and air will now catch fire, and we shall have two flames, one above and the other below the gauze, quite distinct from each other.

2. Put out the gas flame by pinching the india-rubber supply-tube: lay the wire-gauze upon the mouth of the burner, and again allow the gas to flow. Hold a lighted match just above the gauze; the gas passing through the gauze will catch fire, as in the last experiment. Now raise the wire-gauze gradually; the burning gas will not pass downwards through it, and the flame may be lifted 5 cm. or more from the jet, leaving a clear flameless interval between them.

Luminosity of Flames.

Most light-giving flames owe their brightness not to the glowing molecules of the gases themselves, but to the presence in them of strongly-heated solid particles, which emit light at a much lower temperature than the molecules of a gas. To illustrate this —

(a) Hold a bit of platinum foil or iron wire in the non-luminous flame of a Bunsen burner; it cannot be hotter than

the gases which surround it, and yet it emits a great deal of light, becoming 'white-hot,' as we say.

(b) Take two bits of charcoal and rub them together close to one of the air-holes at the bottom of the burner, so as to grind off a number of fine particles of charcoal. These will be driven into the tube by the stream of in-rushing air, and will become ignited when they reach the flame, rendering it comparatively bright.

(c) Place two small tufts of cotton wool at a little distance from each other on a plate, and pour upon each a few drops of common alcohol. Pour upon *one* of the tufts a few drops of turpentine also, and then set fire to both of them. Notice that the alcohol burns with a flame which is only faintly luminous, while the mixture of alcohol and turpentine gives a bright, white, rather smoky flame. The difference between the two cases is this—alcohol contains comparatively little carbon combined with hydrogen and also oxygen, while turpentine contains a great deal of carbon combined with hydrogen only. When alcohol is burnt in air, the carbon in it finds an ample supply of oxygen, together with what it obtains from the air, to combine with, and form carbon dioxide; and so none is separated as carbon in the flame. Turpentine, on the other hand, contains so much carbon that the supply of oxygen obtained from the air is not sufficient to combine with the whole of it; therefore some is separated in a solid form, and these particles, being heated to whiteness, render the flame bright. A similar explanation, it will be remembered, applies to the case of the flame of ethylene (p. 203), and of coal-gas (p. 4).

Combustion of Air in Coal-gas.

Since combustion is, as has been explained, simply a combination of one substance with another, it clearly does not matter (so far as the fact of chemical action is concerned) in what way the two things come into contact. Usually, a stream of gas issues into a large mass of surrounding air, and combustion takes place where they mix. Hence we call coal-gas in ordinary

phrasology a 'combustible' gas, and air a 'supporter of combustion.' But we may easily reverse the conditions and surround a jet of air with an atmosphere of coal-gas; and combustion should (on the theory already given as to its nature) take place equally well close to the jet. The experiment may be made as follows:—

Take a paraffin-lamp glass of the usual shape (shown in fig 84), about 20 cm. high, and fit a cork to its lower and wider end. Into

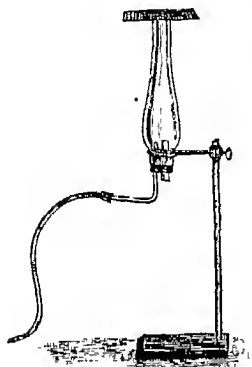


Fig. 84.

the centre of this cork fit a short piece of glass or brass tubing about 5 cm. long and 12 mm. in internal diameter (a piece cut from a small test tube will do, but thin brass is preferable); the end of this should project about 3 cm. within the lamp-glass. Fit also into the cork, by the side of the central tube, a short elbow-tube, so that the end may project very slightly through the cork within the lamp-glass. Support the lamp-glass thus fitted in a retort-stand, as shown in fig. 84, and connect the end of

the elbow-tube with the gas supply by a piece of india-rubber tubing. Lay upon the top of the lamp-glass a piece of fine wire-gauze about 12 cm. square (not less), and turn on the gas. In about half a minute the glass will be full of gas, and the latter may be lighted at the top of the gauze, showing the usual flame of coal-gas burning when surrounded by air. The gas supply should be adjusted so as to give a flame about 20 cm. high (not less).

Now pass a lighted match or taper quickly up the short central tube fitted through the cork; a flame will appear at the top of the tube within the lamp-glass, which is that of air burning in coal-gas.

Thus we have the two combustions under exactly reversed conditions taking place simultaneously.

[It will be advisable to turn off the gas as soon as the above phenomena have been well observed, to avoid risk of cracking the glass.]

Additional Experiments.

Sensitive Flames.

It has been already seen, when the properties of hydrogen were being examined, p. 134, that a flame formed by gas burning at a jet is, when the supply of air to it is rather limited, subject to such quick alterations of form and size as to throw the surrounding air into vibration and produce a musical note. A similar unsteadiness of the flame may be produced in the reverse way, *viz.* by throwing the air round it into vibration so as to baffle the rush of gas from the jet. The most striking forms of these 'sensitive flames' are obtained by employing a specially-constructed jet and forcing through it gas under high pressure, but a very fairly sensitive flame may be produced in the following way.

Attach the mouth blowpipe to a piece of india-rubber tubing connected with the gas supply, and fix it horizontally in a Bunsen's holder, in the position shown in fig. 64, p. 93, with the jet pointing straight upwards. Lay a piece of fine wire-gauze on the largest ring of the retort-stand and support it just over the up-turned jet, leaving an interval of 1 or 2 mm. between the jet and the gauze. Turn on the gas and light it above the gauze; then loosen the screw of the retort-ring and gradually raise the gauze higher and higher until the flame, hitherto steady, shows a tendency to flutter and sink down upon the gauze. The latter should be raised as high as possible above the jet, consistently with the flame burning steadily while undisturbed, and the retort-ring should be fixed in this position.

The flame will now probably be found sensitive to some sounds, such as a hiss or the rattle of a bunch of keys near it, shrinking suddenly close to the gauze and giving a roaring sound. If this is not the case at first, raise or lower the gauze until the best result is obtained.

If a pitch-pipe, or other similar instrument is at hand, the effect of various musical notes on the flame may be tried, and it will be found much more sensitive to some than to others.

The effect is due to the agitation of the air between the jet and the gauze, which causes irregularity in the passage of the gas through the meshes of the gauze, and therefore unsteadiness in the flame on the upper surface.

COMPOUNDS OF CARBON WITH HYDROGEN AND OXYGEN.

These constitute the majority of what are called 'organic' substances; a term which may be explained to mean, substances derivable from plants or animals. Only a few typical examples of radicles belonging to this class will be examined here; those being selected which the student is most likely to meet with in the ordinary course of elementary work.

17. ACETATES.

	Formula of molecule.
[Typical examples,—Hydrogen acetate,	$H(C_2H_3O_2)$
Lead acetate,	$Pb(C_2H_3O_2)_2$

These are principally formed in the last stage of the fermentation of beer, wine, &c.; the alcohol undergoing a further change, owing to the action of the oxygen of the air, and becoming sour from the formation of hydrogen acetate, which is common vinegar or acetic acid.

Another source of them has been already illustrated, p. 183, viz. the decomposition of woody fibre by heat, when acid vapours of hydrogen acetate were found among the products.

Properties of Acetates.

*1. When strongly heated they become charred.

Put a small bit of lead acetate into an ignition-tube and heat it in the flame of a Bunsen's burner. It will first melt, then give off its water of crystallisation, and on being still further heated it will turn black owing to separation of carbon, while strongly smelling vapours of acetone and other products will be given off.

*2. When heated with hydrogen sulphate, they give off vapours of hydrogen acetate.

Place a small quantity of lead acetate in a test-tube, pour on it 2 or 3 c.c. of strong hydrogen sulphate, and heat it gently. The substance will not blacken (as a tartrate does), but pungent-smelling vapours of hydrogen acetate will be given

off, which will redden a piece of litmus-paper held within the mouth of the tube.

[If time permits, a little hydrogen acetate may be prepared from lead acetate in an apparatus similar to that which was used for the distillation of hydrogen nitrate (p. 157), 20 grms. of lead acetate (or, better, sodium acetate) being taken instead of potassium nitrate.]

***3. When heated with alcohol and hydrogen sulphate, they yield fragrant-smelling ethyl acetate.**

Add some hydrogen sulphate to a little lead acetate, as in the last experiment; then add two or three drops of pure alcohol (rectified spirits of wine, not methylated) and warm gently. Vapours of ethyl acetate (acetic ether) will be given off, which possess a characteristic fragrant smell, not unlike that of fresh apples (best observed after closing the mouth of the tube with the finger, and slightly shaking the warm liquid).

[A comparative experiment should be made by heating a little of the alcohol alone with hydrogen sulphate in order to discriminate between the slight smell of the ethylene thus formed and the much stronger and sweeter smell of ethyl acetate.]

***4. Their neutral solutions, when tested with iron perchloride, give a dark red colour, and, on being boiled, a red precipitate.**

Put five or six drops of hydrogen acetate (or solution of lead acetate) into a test-tube, add 4 or 5 c.c. of water and a small quantity of finely-powdered chalk. Boil the mixture for half a minute, and filter it into another test-tube. A neutral solution of calcium acetate will be thus obtained, by double decomposition. Add to the clear filtrate one drop (not more), taken up on a glass rod, of solution of iron perchloride; the liquid will turn red owing to formation of iron acetate. Lastly, boil the solution; it will get darker in colour, and soon a reddish precipitate will form. This consists of 'basic iron acetate'¹.

¹ Many such basic acetates are known; for instance, basic copper acetate ('verdigris'). They may be regarded as formed by the action of water on the ordinary salt: the hydrogen of the water takes out and combines with some of the acetate radicle, forming hydrogen acetate, while the oxygen of the water takes the place of this radicle in the salt.

In applying this reaction in testing for acetates, it should be borne in mind (1) that the iron perchloride must *not* be in excess, (2) that solution of iron perchloride itself gives, on being heated, a red colour and a slight reddish precipitate (unless a good deal of free acid is present). The characteristic points are, the appearance of a red colour in the cold neutral solution, and the complete precipitation of the iron on boiling, leaving a colourless solution.

18. TARTRATES.

	Formula of molecule.
[Typical examples,—Hydrogen tartrate,	$H_2(C_4H_4O_6)$
Sodium-hydrogen tartrate,	$NaH(C_4H_4O_6)$]

These occur in grape juice, the crust deposited from wine consisting principally of calcium tartrate.

Properties of Tartrates.

*1. When strongly heated they become charred.

Heat a little solid sodium-hydrogen tartrate in a test-tube nearly to redness, holding the tube with the open end slightly inclined downwards, lest any moisture should run back to the heated part and crack the tube. The substance will become charred, and give off vapours possessing a characteristic smell, like burnt sugar. The residue, besides carbon, also contains sodium carbonate; as may be proved by pouring on it, when cold, a few drops of dilute hydrogen chloride. Carbon dioxide will be evolved, and may be tested for by holding within the tube a pipette dipped in lime-water (p. 195).

*2. When heated with strong hydrogen sulphate, they are decomposed and turn black.

Place a small quantity of solid sodium-hydrogen tartrate in a test-tube, add a little strong hydrogen sulphate, and heat cautiously. The mixture will blacken, owing to the separation of carbon, and give off carbon dioxide and other gases with effervescence.

[For the following experiments a solution of sodium-hydrogen tartrate (1 grm. of the salt dissolved in 25 c.c. of water) should be used.]

***3. When mixed with a potassium salt, their solutions give a white crystalline precipitate.**

Put a little of the solution of sodium-hydrogen tartuate into a test-tube, and add solution of potassium hydrate until it is alkaline to test-paper; then add enough hydrogen acetate to make it decidedly acid, stir the mixture with a glass rod, and shake it for a few seconds. A crystalline precipitate of potassium-hydrogen tartrate will be gradually deposited, the crystals forming first along the lines where the glass rod had rubbed against the surface of the tube¹. If a few more drops of potassium hydrate are added, the precipitate will re-dissolve; hence the reason for acidifying the solution with hydrogen acetate, as above directed.

***4. When mixed with a calcium salt, their solutions give a white precipitate soluble in ammonium chloride.**

To another portion of the solution of sodium-hydrogen tartrate add at least three or four times its volume of lime-water. A white precipitate of calcium tartrate will be produced, which will dissolve on addition of a few drops of solution of ammonium chloride.

***5. They readily reduce silver salts.**

Add to another portion of the solution enough solution of sodium carbonate to make it strongly alkaline; and then add a drop of solution of silver nitrate, which will produce a white precipitate of silver carbonate and tartrate. Lastly, heat the mixture to boiling, adding a little more silver nitrate if the precipitate re-dissolves. The precipitate will turn black owing to its reduction to metallic silver.

This reducing action of tartrates (in which the carbon and hydrogen of the radicle both combine with oxygen) is applied in processes for silvering glass, as will be more fully explained under SILVER.

¹ This should be especially noticed as an effective method of promoting the formation of a crystalline precipitate. The contact of the rod with the glass alters the surface in some way so as to form nuclei to which crystals will attach themselves.

19. OXALATES.

	Formula of molecule.
[Typical examples,—Hydrogen oxalate,	$\text{H}_2\text{C}_2\text{O}_4$
Potassium oxalate,	$\text{K}_2\text{C}_2\text{O}_4$
Ammonium oxalate,	$(\text{H}_4\text{N})_2\text{C}_2\text{O}_4$]

These occur in the sap of many plants, especially wood-sorrel (*oxalis acetosella*), and the common rhubarb, which owe their sour taste to the hydrogen oxalate (oxalic acid) which they contain. Hydrogen oxalate is formed in the action of hydrogen nitrate on starch, already tried in the preparation of nitrogen trioxide, p. 167. Potassium oxalate, from which all the other oxalates are obtainable, is now usually prepared by the action of potassium hydrate (caustic potash) upon sawdust.

The formation of an oxalate by this method may be illustrated on a small scale as follows. Put about 5 grms. of potassium hydrate into an iron cup (fig. 8, p. 7), add about 3 c.c. of water, and place it on a piece of wire-gauze over an argand burner to dissolve. Put into the solution about 1 grm. of tow (which has the same chemical composition as wood), made into a small ball, and press it down with a glass rod that it may become thoroughly soaked. Heat the mixture carefully, with constant stirring, until the water is all driven off and the tow is reduced to a light brown, pasty mass. Hydrogen gas is given off, as may be proved by bringing a lighted match just above the froth¹. Continue the heat, with stirring, until the residue is quite dry, taking care not to raise the temperature so far as to char the mass; then leave it to cool while other experiments are proceeded with. Finally boil the residue with about 10 c.c. of water, filter the solution, and evaporate it to the crystallising point: i. e. until a drop placed on a watch-glass and stirred deposits crystals (p. 62). It should then be set aside for some hours: crystals of potassium oxalate will be formed, which may be separated by pouring the contents of the dish on a filter.

They should be proved to consist of an oxalate by dissolving some of them in water and applying tests 3 and 4.

¹ The reaction is not a very definite one. The formula of a molecule of woody fibre, such as tow or sawdust, is probably $\text{C}_6\text{H}_{10}\text{O}_6$, so that in order to convert it into potassium oxalate ($\text{K}_2\text{C}_2\text{O}_4$) hydrogen must be removed and oxygen and potassium added. Hydrogen is given off during the action, and the potassium hydrate (KHO) yields oxygen and potassium.

• Properties of Oxalates.

[For some of the following experiments a solution of ammonium oxalate may be used, containing 1 *gram.* of the salt in 30 c.c. of water.]

***1. When strongly heated, they are decomposed (but without decided charring), yielding a carbonate.**

Put a little potassium oxalate, or calcium oxalate¹, into a small test-tube and heat it nearly to redness. Only a slight darkening or charring will be noticed, while carbon monoxide will be given off and may be tested for with a lighted match². When the residue in the tube is cool, pour on it a little dilute hydrogen chloride; carbon dioxide will be given off with effervescence, showing that a carbonate has been formed.

There are one or two oxalates which behave in a different way when heated. Thus hydrogen oxalate volatilises almost unaltered when carefully heated.

Place a few crystals of hydrogen oxalate in a small test-tube, and heat them slowly. The salt will melt and give off its water of crystallisation, which should be prevented from condensing by warming the whole of the tube (held in a paper holder, p. 68). Finally, on slightly increasing the heat, the hydrogen oxalate will sublime unaltered, condensing in long prismatic crystals.

Ammonium oxalate also volatilises entirely, but is in great part decomposed, yielding white fumes of a substance called oxamide.

2. When heated with strong hydrogen sulphate they are decomposed, with evolution of both the carbon oxides.

Pour 3 or 4 c.c. of strong hydrogen sulphate on a few crystals

¹ This may be prepared, if none is at hand, by heating about 6 or 8 c.c. of solution of ammonium oxalate nearly to boiling, and adding about the same quantity of solution of calcium chloride (also heated). Boil the liquid for a few moments, to promote the separation of the precipitate; then filter it, and wash and dry the precipitated calcium oxalate as already directed, p. 92. If the precipitate passes through the filter, as it is rather apt to do unless separated from boiling solutions, a filter of Swedish paper must be used.

²

Calcium oxalate.		Calcium carbonate.		Carbon monoxide.
CaC_2O_4	=	CaCO_3	+	CO

of hydrogen oxalate in a test-tube, and heat the mixture cautiously. Carbon dioxide and carbon monoxide will be given off with effervescence. (Compare the method of making carbon monoxide, p. 197.) The latter gas will burn with its characteristic blue flame if a lighted match be held to the mouth of the tube; the presence of the former gas may be shown by holding a pipette dipped in lime-water within the test-tube (see p. 195).

***3. They are readily decomposed by oxidising agents, e.g. manganese dioxide, with formation of carbon dioxide.**

Place a little manganese dioxide in a test-tube, add enough water to cover it, and then a few drops of strong hydrogen sulphate. If there should be any effervescence (manganese dioxide sometimes contains carbonates), wait until this has ceased, and then add a few drops of a solution of ammonium oxalate. Carbon dioxide will now be given off with effervescence (which will be best detected by its sound, the tube being held to the ear), and should be tested for with lime-water in a pipette, as above.

***4. Tested with calcium sulphate, their solutions (if neutral or alkaline) give a white precipitate, insoluble in hydrogen acetate, but soluble in hydrogen chloride.**

Add 5 or 6 c.c. of solution of calcium sulphate to some of the solution of ammonium oxalate, made alkaline with ammonia. A white precipitate of calcium oxalate will be formed.

(a) Pour off about half of the liquid, containing the precipitate in suspension, into another test-tube, add a little hydrogen acetate, and warm slightly. The precipitate will remain undissolved.

(b) To the remainder of the liquid add some dilute hydrogen chloride, and warm. The precipitate will dissolve, but without effervescence (differing in this respect from calcium carbonate).

It will be advisable at this stage of chemical work, to apply the knowledge already gained of the properties of some of the non-metallic radicles to their detection in a substance of

unknown composition. This process, which is called 'Analysis' in a narrow, technical sense, and the principles of which will be more fully explained in the introduction to Part II, consists in the application of tests in a certain definite order to the substance under examination, in order to find out which of the known radicles it agrees with in properties.

A short course of experiments, applicable to the detection of the radicles already treated of, will be found in Appendix C; and the student is advised to take at least four or five solutions of which nothing is known but that they contain some one of these radicles (associated with a metal, such as potassium, which will not interfere with the tests), and to find out which radicle is present by the methods there given.

COMPOUND OF CARBON WITH NITROGEN.

20. CYANOGEN AND ITS COMPOUNDS.

[Formula of molecule, $(\text{CN})_2$ or Cy_2

Weight " „ 52 hydrogen-atoms.]

[This gas and its compounds are extremely poisonous, and great care is necessary in experimenting on it and them. The vapours of cyanogen and hydrogen cyanide (prussic acid) should not be inhaled more than is necessary for recognising their presence; not a particle of a cyanide should be allowed to get into a scratch or cut; and the room in which the experiments are made should be well ventilated. Every good laboratory has a 'draught-cupboard,' having a glass sliding front, and connected with a chimney or flue in which a strong upward draught is maintained by a ring of gas-jets or otherwise. Experiments involving the production of cyanogen or hydrogen cyanide should be performed in such a cupboard, if possible.]

Cyanogen is of interest as being the first compound substance which was recognised as a radicle from its property of behaving in chemical actions as if it was an indivisible element. It is obtained by the action of heat on some of the cyanides, which are compounds of it with other radicles; and the mode

of formation of these will be described before the examination of the properties of cyanogen itself.

Formation of Cyanides.

Formula of molecule.

[Typical examples,—Potassium cyanide, KCN or KCy
Hydrogen cyanide, HCN or HCy
Iron protocyanide, $\text{Fe}(\text{CN})_2$ or FeCy_2
Mercury cyanide, $\text{Hg}(\text{CN})_2$ or HgCy_2]

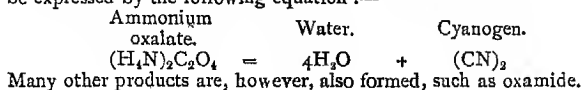
The practical source of all the compounds of cyanogen is the decomposition by heat of organic substances containing nitrogen, such as leather, horns, or horsehair. It has been seen already, p. 146, that when such substances are heated alone, the nitrogen unites with hydrogen, and ammonia is formed; but when a substance (such as potassium or a compound of it) which can unite with cyanogen is present, then some at any rate of the nitrogen combines with carbon to form cyanogen, which immediately combines with the potassium, producing potassium cyanide: and from this latter salt various other cyanides are obtainable.

The process by which a compound of cyanogen is manufactured on the large scale (*viz.* by fusing together skins, horn, &c., potassium carbonate, and iron filings) is hardly adapted for a laboratory experiment; but the principle on which cyanides are formed may be shown in the following way.

Ammonium oxalate contains the same elements as skin and horn, *viz.* carbon, nitrogen, hydrogen, and oxygen, and when it is strongly heated with potassium hydrate, potassium cyanide is formed in the manner above explained¹.

Powder a small bit of potassium hydrate, about half the size of a pea: add to it rather more than twice as much ammonium oxalate (roughly measured), and grind the whole together till thoroughly mixed. Fill the bulb of an ignition-tube with the mixture and heat it over a lamp. The tube should be held with crucible tongs, and

¹ The reaction, so far as the production of cyanogen is concerned, may be expressed by the following equation:—



the whole of it warmed, to avoid condensation of water, which might crack it. Continue heating the mixture carefully until it has turned quite black; then dip the bulb, while still hot, into 2 or 3 c.c. of water placed in a porcelain dish, when it will crack to pieces and the water will dissolve the potassium cyanide out of the residue. The liquid should be warmed and filtered, while the other experiments with cyanides are being made: the presence of a cyanide in it may then be proved by applying test 3, p. 226.

Formation of Ferrocyanides.

Formula of molecule.

[Typical examples,—Potassium ferrocyanide, $K_4(FeCy_6)$

Iron ferrocyanide, $Fe_4(FeCy_6)_3$]

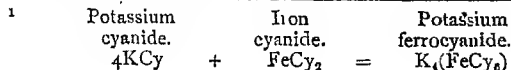
These are salts containing the ferrocyanogen radicle, which (as seen from the above formulæ) consists of iron associated with carbon and nitrogen in the same proportions as in cyanogen. Potassium ferrocyanide (the common 'prussiate of potash') is formed when iron protocyane is mixed with excess of potassium cyanide, the iron no longer acting as a metallic or electro-positive radicle, but becoming part of the electro-negative radicle, ferrocyanogen.

1. Potassium ferrocyanide.

Make a strong solution of potassium cyanide by dissolving 1 gm. of the salt in 5 c.c. of water, and add to it one drop (not more) of solution of iron protosulphate. A precipitate of iron protocyane will be at first formed, but this, on shaking and warming the mixture, will be redissolved, giving a yellow solution of potassium ferrocyanide¹. Filter the solution from any slight flocculent residue, and use it in the next experiment.

2. Iron ferrocyanide.

Add to the solution of potassium ferrocyanide just obtained sufficient hydrogen chloride to make it strongly acid; then add a drop of solution of iron perchloride. A deep blue precipitate of iron ferrocyanide will be formed, which is the common paint known as 'Prussian blue.'



Formation of Cyanates.

[Typical example,—Potassium cyanate, K(CNO)]

Formula of
molecule.

In the cyanate radicle, cyanogen is associated with oxygen, and this combination is readily effected by fusing a cyanide with any substance capable of giving up oxygen. In fact, potassium cyanide is a very powerful reducing agent, and is used for that purpose in blowpipe experiments.

Mix together 2 grms. of potassium cyanide and 4 grms. of lead protoxide (litharge), and heat them strongly in an iron spoon over the Herapath's blowpipe, stirring the mixture with a piece of iron wire. The potassium cyanide combines with the oxygen of the lead oxide, forming potassium cyanate, while the lead separates in the metallic form, appearing as a large bright globule under the layer of fused salt.

Pour the contents of the spoon upon a clean plate of iron (such as a sandbath). When cold the mass may be warmed with water in a beaker, when the globule of lead will be left undissolved, and a solution containing potassium cyanate will be obtained.

Formation of Thiocyanates

(formerly called Sulphocyanates).

[Typical example,—Potassium thiocyanate, K(CNS)]

Formula of
molecule.

These are very analogous to the cyanates (as seen by the formula), but contain sulphur in place of oxygen, hence the name thiocyanate (from *θειον*, *sulphur*). They are formed whenever a cyanide is heated with sulphur or a substance which yields sulphur.

1. Potassium thiocyanate.

Put a little potassium cyanide into the bulb of an ignition-tube, add a minute fragment of sulphur, and fuse the mixture over a Bunsen's burner. Dip the bulb while still hot into a little

water in a porcelain dish, so as to crack it and allow the mass of potassium thiocyanate to dissolve in the water. Pour the solution into a beaker, and keep it for the next experiment.

2. Iron thiocyanate.

Add to the solution of potassium thiocyanate, just obtained, enough dilute hydrogen chloride to make it strongly acid; then fill up the beaker with water and add a drop of solution of iron perchloride. Iron thiocyanate will be formed, which is of an intense red colour, as will be seen even in so very dilute a solution.

Properties of Cyanides.

[For the following experiments a solution of potassium cyanide may be used, containing 1 gram. of the salt dissolved in 80 c.c. of water.]

*1. When heated with hydrogen sulphate, they give off hydrogen cyanide.

Add a few drops of strong hydrogen sulphate to some solution of potassium cyanide and warm the mixture. Hydrogen cyanide will be given off with slight effervescence, and may be recognised by its peculiar smell, resembling that of essence of almonds (which, in fact, is liable to contain this very poisonous acid, unless carefully purified). Solid potassium cyanide has a similar smell, being easily decomposed, even by the carbon dioxide in the air.

*2. Their solutions, when tested with silver nitrate, give a white precipitate, soluble in ammonia, and decomposable by hydrogen nitrate.

Add one drop of solution of silver nitrate to some solution of potassium cyanide. A white, curdy precipitate (of silver cyanide) will be produced, which will redissolve on agitation. Add more silver nitrate until a permanent precipitate is produced; then pour off half of the liquid (containing some of the precipitate in suspension) into another tube.

(a) To this portion add some solution of ammonia and warm. The precipitate will readily dissolve, but will be formed

again on adding sufficient dilute hydrogen nitrate to neutralise the excess of ammonia.

(b) Allow the other portion of the precipitate to subside, pour off the liquid, retaining the precipitate in the tube, and boil the latter with a little strong hydrogen nitrate. The silver cyanide will be slowly decomposed and dissolved by the acid. You may, without waiting until it has all dissolved¹, prove the presence of silver in the solution by pouring it into another tube, and adding a drop or two of dilute hydrogen chloride, when a white precipitate of silver chloride will be formed.

***3. Their solutions, when mixed with potassium hydrate and iron protosulphate, yield a ferrocyanide.**

This action has been explained already, p. 223; and it affords a means of detecting very small quantities of a cyanide, since a mere trace of a ferrocyanide may be recognised by the formation of 'prussian blue' on addition of iron perchloride.

The best way of applying this test is as follows.

Add to some solution of potassium cyanide two or three drops of solution of potassium hydrate, and then about the same quantity of solution of iron protosulphate, and shake the mixture thoroughly, warming it gently. A dull greenish precipitate, consisting of a mixture of iron protohydrate and perhydrate, will be formed. Now add an excess of dilute hydrogen chloride (sufficient to make the liquid strongly acid); a deep blue precipitate will be formed.

[The delicacy of the test may be shown by repeating the experiment, using only one drop of the solution of potassium cyanide diluted with 5 or 6 c.c. of water. Even in this case the liquid will be coloured distinctly blue.]

The changes which occur are of the following nature:—On addition of the iron protosulphate a portion of iron cyanide is formed; this unites with the rest of the potassium cyanide to form potassium ferrocyanide (p. 223). At the same time, a mixture of iron protohydrate and perhydrate (the latter formed by

¹ Potassium cyanide often contains a chloride, and in this case a residue of silver chloride would remain, undecomposable by hydrogen nitrate.

the action of the oxygen of the air) is precipitated by the action of the potassium hydrate on the excess of iron sulphate. When hydrogen chloride is added, it dissolves these hydrates, and the iron perchloride formed acts upon the potassium ferrocyanide to form the deep blue precipitate of iron ferrocyanide.

*4. When heated with a sulphide, they form a thiocyanate.

This is another very delicate test for the presence of a cyanide; since the presence of a thiocyanate can be readily detected by the red colour formed on addition of iron perchloride (p. 225).

Pour one or two drops of solution of potassium cyanide into a porcelain dish, add a drop of solution of yellow ammonium sulphide, and evaporate the mixture to dryness. The potassium cyanide will unite with the sulphur present in the ammonium sulphide, forming potassium thiocyanate.

Add to the residue a few drops of dilute hydrogen chloride and then one drop of solution of iron perchloride. Iron perthiocyanate will be formed, which will colour the liquid deep red.

Additional Experiments.

Preparation of Cyanogen.

[The remarks on the poisonous nature of this gas, p. 221, should be referred to.]

Cyanogen is obtained in a pure state by the decomposition of certain of the cyanides, preferably mercury cyanide. When this salt is heated, it breaks up into the two radicles it contains, *viz.* mercury and cyanogen (compare the decomposition of mercury oxide by heat, p. 77).

[If mercury cyanide is not at hand, a mixture of mercury chloride and potassium ferrocyanide (which yields mercury cyanide by double decomposition) may be used instead; which may be made in the following way:—

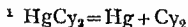
Reduce about 2 grms. of potassium ferrocyanide to fine powder, and heat it in a porcelain dish on a sandbath, with constant stirring, until all the water of crystallisation has been driven off. (This may be known by holding a cold watch glass just above the salt; if moisture is deposited,

the dehydration is not complete.) Weigh out 1 grm. of the dried salt, and 1 grm. of mercury perchloride ('corrosive sublimate'); mix them thoroughly in a mortar, and use the mixture as directed below]

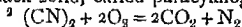
Powder 1 grm. of mercury cyanide, dry it thoroughly in a dish on the sandbath, and put it into a small, perfectly dry test-tube. Fit a cork to the tube, and pass through the cork the glass jet already made (p. 32), the wide end of the tube being outwards (since cyanogen burns best at a rather wide opening). Support the test-tube slanting in a Bunsen's holder and heat it moderately over an argand burner. The mercury cyanide is decomposed into mercury, which condenses in bright drops on the side of the tube, and cyanogen, which escapes as gas¹.

After the action has begun, and the peculiar, penetrating smell of cyanogen has been noticed (most safely by wafting with the hand a very little of the vapour towards your face), apply a light to the end of the tube. The cyanogen will take fire, burning with a fine purple flame. Hold a small gas bottle over the flame for a few seconds; no moisture will be deposited, but on pouring a little lime-water into the bottle and shaking it up, the cloudiness will prove that carbon dioxide is produced during the combustion, nitrogen being the only other product².

Observe what this expt., together with the similar one made with ethylene (p. 203), prove with regard to the relative affinity of oxygen for hydrogen, carbon, and nitrogen respectively. In the combustion of ethylene the oxygen united with all the hydrogen but with only some of the carbon. In the case of cyanogen, the oxygen united with all the carbon but none of the nitrogen. The conclusion is obvious.



A portion of the cyanogen remains behind in a different condition, as a black solid, called paracyanogen (C_3N_3).



21. CHLORINE.

[Symbol of atom,	Cl
Weight ,,	35.5 hydrogen-atoms.
Formula of molecule,	Cl ₂
Weight ,,	71 hydrogen-atoms.]

Preparation of Chlorine.

Apparatus required.—Flask, elbow-tubes, and cork-joint used in Ex. 12; argand burner; wooden blocks; card; one large and six small gas bottles; taper on wire; deflagrating cup; crucible tongs; beaker; porcelain dish; one large and one small cylindrical gas jar; glass disc; supplementary pan of the pneumatic trough; scales and weights.

Sodium chloride (common salt); manganese dioxide; strong (common) hydrogen sulphate; blue litmus-paper; solution of indigo sulphate; phosphorus; Dutch gold-leaf, or metallic antimony (or brass filings); turpentine; strip of coloured calico; solution of potassium hydrate.

[We have in this case to deal with a gas which is soluble to a considerable extent in water, though much less so than ammonia or hydrogen chloride. Its solubility rapidly diminishes as the temperature of the water is raised, and hence it may be collected without much loss over warm water, the ordinary pneumatic trough being employed. But its density is so high that it can be most readily collected by downward displacement, like carbon dioxide.

Its action on the lungs is so extremely irritating and injurious that it should never be prepared in a room which cannot be thoroughly ventilated. All the experiments should be performed in a 'draught-cupboard' (p. 221), if possible; and, in default of this, a shed out of doors is the best place for the work. If, however, the chlorine must be prepared in a room, observe (1) to collect it over warm water, not by displacement; (2) to allow *none* to escape into the air unnecessarily¹; (3) as soon as the experiments are performed, to throw away the water in the trough, and wash it and the bottles at once with clean water containing a little sodium carbonate ('washing soda').

¹ The first portions of the gas, which come over mixed with air, should be collected in a large gas bottle; into this, when full, some solution of caustic soda should be poured (a bit of paper being put between the stopper and neck of the bottle), and shaken up in the gas until the smell of chlorine has disappeared. Or, the bottle may be taken out of doors and left open for some minutes.

A little ammonia sprinkled on a warm plate is the best means of getting rid of the gas. If the lungs are affected, pour a little pure alcohol into a test-tube, warm it, and inhale the vapour.]

The chief source of this element is common salt, which contains chlorine united with sodium. In order to obtain chlorine from salt it is not sufficient to add an acid, since the chlorine unites at once with the hydrogen of the acid, forming hydrogen chloride. But if we add to this latter a substance which readily gives up oxygen, e.g. manganese dioxide, the oxygen unites with the hydrogen, and chlorine is set free. To illustrate this—

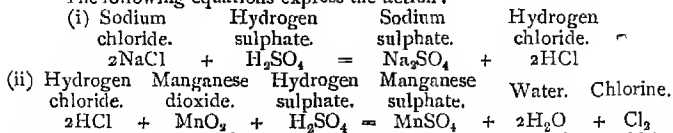
Put a little sodium chloride into a test-tube and pour on it some strong hydrogen sulphate. A brisk action will begin, and a colourless, pungent-smelling gas will be given off, which reddens a strip of moist litmus-paper held in the tube. This gas is hydrogen chloride, and its properties will be more fully considered in the next Exercise.

Now add a little manganese dioxide, and warm slightly. A greenish-yellow gas will soon fill the tube, which has a most irritating and suffocating smell, and which bleaches a strip of moist litmus-paper. This gas is chlorine¹.

Measure 40 c.c. of water into a beaker capable of holding 100 c.c., placed on a plate, and add to it by degrees 40 c.c. of strong common hydrogen sulphate. While the mixture is cooling, weigh out 25 grms. of common salt (sodium chloride) and an equal quantity of manganese dioxide, and mix them together.

Arrange an apparatus like that used for carbon dioxide (fig. 81, p. 188)², put the mixture into the flask and add the diluted

¹ The following equations express the action:—



² If the gas is required to be quite pure, a small wash-bottle should be interposed between the flask and the delivery tube, partly filled with plain water, to retain any hydrogen chloride which may come over.

acid through the funnel: then shake the flask until the contents are thoroughly mixed. Place the whole apparatus in the draught cupboard, and apply a very gentle heat. Collect one large and six small bottles of the gas (remembering to keep the door of the draught cupboard closed as much as possible, so that none of the gas may escape into the room). The yellowish-green colour of the gas will sufficiently show when the bottles are full, especially if a sheet of white paper is held behind each bottle while the gas is passing into it. The colour is well seen by the faint bluish light of the flame of a Bunsen's burner.

When the bottles are all filled, pass the gas into about 30 c.c. of solution of potassium hydrate placed in a large test-tube (noting its ready and complete absorption by the potash with formation of potassium hypochlorite, as more fully explained in Exercise 23), until the liquid acquires a yellow colour and the gas is no longer absorbed. It should then be reserved in a closely-corked tube or bottle for use in Exercise 24.

If the gas is still coming off (the end of the action may be known by the mixture in the flask becoming reddish brown) pass it into a bottle or flask filled with water, to form the solution of chlorine which is used as a test in analytical work¹.

[Put away one of the small bottles of chlorine in a dark cupboard for use in Exercise 23.]

[Another good method of preparing chlorine is to heat a mixture of 60 c.c. of strong hydrogen chloride with 20 grms. of manganese dioxide. In this case, however, half the chlorine is retained in combination with manganese².]

Properties of Chlorine.

[All the experiments should be made in a draught cupboard, if possible.]

*1. Its suffocating smell and its yellowish green colour will have been noticed already.

¹ Fuller directions for making this solution will be found in Appendix B.

² Hydrogen chloride. Manganese dioxide. Manganese chloride. Water. Chlorine.
 $4\text{HCl} + \text{MnO}_2 = \text{MnCl}_2 + 2\text{H}_2\text{O} + \text{Cl}_2$

2. Its density, nearly $2\frac{1}{2}$ times that of air.

This has been proved by the mode of collecting it, and will be further illustrated in expt. 7.

3. Its solubility in water.

Pour about 20 c.c. of water into a small bottle of chlorine; insert a bit of paper between the stopper and the neck, invert the bottle, and shake it for a few seconds. The water will readily dissolve the gas, as will be proved by its acquiring the colour and smell of chlorine, and by the bubbles of air which enter the bottle.

***4. Its bleaching action on indigo, litmus, and other colouring matters.**

(a) Add a little of the solution of chlorine made in the last experiment to some dilute solution of indigo sulphate (about 3 drops of the strong solution in 10 c.c. of water). The blue colour will be at once destroyed.

(b) Put into the bottle containing the solution of chlorine, a strip of blue litmus-paper, a flower, a bit of coloured calico or cloth, and a bit of paper having some printed words upon it and also some words written with common ink. The colour will be more or less quickly discharged in all cases, except that of the printer's ink: this consists of carbon, for which chlorine has very slight affinity.

5. Its relation to ordinary combustion.

Immerse a lighted taper in a small bottle of chlorine. It will not be extinguished, but will burn with a dull smoky flame, depositing abundance of soot; and the gas itself will not catch fire.

Observe that you have here combustion taking place in a gas which contains no oxygen. In fact, although oxygen usually takes part in combustion, it is not (as was formerly thought) necessary. The phenomena of combustion are simply due (as already mentioned, p. 208) to the light and heat given off during violent chemical action. In the present case the chlorine combines with the hydrogen of the candle, while the carbon, for which it has only a slight affinity, remains quite unaltered (see also expt. 9).

6. Its combination with non-metals, such as phosphorus.

Cut from a stick of phosphorus a small piece about half as large as a pea, observing the precautions given on p. 81. Dry it thoroughly on blotting-paper, pressing, but not rubbing it; place it in a deflagrating cup, and immerse it in the large bottle of chlorine. It will catch fire spontaneously, burning with a greenish flame; and a yellowish crystalline deposit of phosphorus pentachloride will be formed in the bottle.

7. Its combination with metals.

Place two or three pieces of Dutch gold-leaf (an alloy of zinc and copper) in a cylindrical gas jar, and invert over them a bottle of chlorine, resting its neck on the mouth of the jar. The heavy gas will quickly descend, and when it reaches the leaves they will catch fire, burning with a dull glow, and forming zinc and copper chlorides.

[If Dutch metal is not at hand, the following experiment may be substituted.

Pour into a bottle of chlorine just enough water to cover the bottom¹. Place some metallic antimony reduced to fine powder in a mortar, in a paper gutter, and shake the substance little by little into the bottle. The metal will catch fire and burn brilliantly when it comes into contact with the gas, forming antimony perchloride.]

8. Its combination with hydrogen.

(a) Suddenly, under the action of heat.

Fill the supplementary pan of the pneumatic trough with warm water. Fill the small stout gas jar with hydrogen gas (from a gas-holder or by the method given on p. 181, note), and decant its contents into a larger gas jar, placed in the pan of warm water. Next, fill the same jar with chlorine from one of the small bottles of the gas, and add it to the hydrogen in the larger jar². You have now a mixture of equal volumes of hydrogen and chlorine.

¹ This is to prevent fracture of the bottle by the burning particles of metal.

² If this is done neatly and rapidly, the loss of chlorine by solution in the water will be very small.

Agitate the jar for a second or two, in order to mix the gases intimately, keeping its mouth below the water-level¹; then transfer some of the mixture to the small jar, remove it to the table and apply a light to its mouth. The gases will unite with explosion, forming hydrogen chloride².

[Another interesting method of causing the sudden combination of hydrogen and chlorine is the action of a bright light. This, although not always successful, since it requires the gases to be mixed in *exactly* the right proportions³, may be attempted as follows.

Have ready at hand a cork rather larger than the mouth of the small gas jar, with one of its ends greased, and also a bit of magnesium ribbon about 12 or 14 cm. long. Decant into a jar, as above, equal volumes (carefully measured) of hydrogen and chlorine, mix them quickly but thoroughly by agitation; then decant some of the mixture into the small jar, close its mouth with the cork (used as a glass disc, i.e. laid on the mouth), and place it mouth upwards on the table. Light the magnesium ribbon, held in the crucible tongs, at a Bunsen's burner, and bring it at once close to the side of the small jar (or take the latter out into full sunshine). An explosion will probably take place, and in any case the union will be quickly effected, white fumes being produced, due to the formation of hydrogen chloride.]

(*b*) Slowly, under the action of a moderate light.

Fill the small jar with the remainder of the mixed gases, close its mouth with a glass plate (greased), remove it from the trough and allow it to remain for at least half an hour in a good diffused light, not in direct sunshine, for fear of an explosion. If you then examine the contents of the jar, you will find that the colour and characteristic odour of chlorine have disappeared, and that the gas fumes in the air, reddens and does not bleach litmus-paper, and possesses the pungent odour of hydrogen chloride.

9. Its action on compounds containing hydrogen.

In most cases such compounds are decomposed, their hydrogen

¹ The gases differ so much in density that their mixture by diffusion alone would be comparatively slow.

² $\text{H}_2 + \text{Cl}_2 = 2\text{HCl}$

³ The chlorine for this experiment should, to ensure its purity, be collected over the pneumatic trough, by displacement.

uniting with the chlorine, for which (as has been proved already) it has a strong affinity. Thus if a strong solution of chlorine in water is exposed to sunlight, oxygen is slowly evolved, and hydrogen chloride is formed in the liquid¹.

The action of chlorine on hydrogen sulphide is precisely similar; sulphur is separated and hydrogen chloride formed, as will be illustrated in expt. 6, p. 273. The value of chlorine as a disinfectant chiefly depends on such decompositions of this and other poisonous gases given off during the putrefaction of organic matter.

The action of chlorine on compounds of hydrogen with carbon is usually, if it takes place at a high temperature, of the same kind. Its effect on ethylene has been illustrated already in experiments 4, 5, p. 204 (these may be tried now, if not then performed). Its action on the hydrocarbon turpentine may be shown as follows.

Pour a few drops of turpentine upon a strip of blotting paper, and plunge it into a bottle of chlorine, leaving the mouth of the bottle open. Dense white fumes will be produced, owing to the formation of hydrogen chloride, and carbon will be deposited: the action being generally so violent as to set the turpentine on fire.

COMPOUNDS OF CHLORINE.

22. CHLORIDES.

	Formula of molecule.
[Typical examples,—Hydrogen chloride,	HCl
• Sodium chloride,	NaCl
Ammonium chloride, (H ₄ N)Cl]	

These are substances containing chlorine united with other radicles. Several examples of their formation have been given

¹ Hence the solution of chlorine required for laboratory purposes should be kept in a bottle made of green glass or covered with opaque paper, or it will soon lose its strength.

in the last exercise; e. g. phosphorus pentachloride, zinc and copper chlorides, and hydrogen chloride.

Preparation of Hydrogen chloride.

Apparatus required.—Flask, elbow-tubes, &c., as used in the preceding Exercise; argand burner; two cylindrical gas jars, 20×5 c.m.; three small gas bottles; tape on wire; two glass discs; porcelain dish; beaker; sandbath; test-tube.

Sodium chloride; common hydrogen sulphate; distilled water; blue litmus-paper; turmeric-paper; solution of litmus.

This substance is usually prepared by the action of hydrogen sulphate on common salt; an action already noticed and explained under CHLORINE, p. 230. The action of the strong acid upon ordinary crystallised salt is so violent that it is necessary to melt the salt previously into compact lumps, so as to expose less surface to the acid¹. If, however, the acid is slightly diluted, the ordinary fine-grained table salt can be used. The gas will not be quite free from moisture, but this is unimportant for most experiments. In preparing and experimenting on it the same precautions should be used as in the case of chlorine, on account of its irritating and corrosive nature.

Measure out 20 c.c. of distilled water into a beaker and add to it gradually 30 c.c. of strong common hydrogen sulphate². Set this aside to cool.

Fit up an apparatus similar to that which was used for preparing carbon dioxide (fig. 81, p. 188), placing a piece of wire-gauze under the bottom of the flask, and fixing it at such a height that the lamp will pass easily under it³. Place in the flask 20 gms. of sodium chloride, and having set a bottle under

¹ This may be done in an iron ladle over a good fire. The salt melts at a red heat, and the liquid should be poured out on a clean piece of iron or slate, and when cold, broken up into lumps about the size of almonds, which should be kept in a well-stoppered bottle.

² The liquid will probably become turbid, for a reason to be explained under SULPHATES, p. 286.

³ If the gas is required to be quite pure, it should be passed through a small wash-bottle containing strong hydrogen sulphate. This dries the gas, and at the same time frees it from any hydrogen sulphate which may be carried over as spray.

the delivery tube, and covered its mouth with a card, pour into the flask the dilute hydrogen sulphate you have just prepared. Apply a gentle heat and fill three small bottles with the gas by displacement, using a lighted taper to ascertain when they are full, precisely as directed in the case of carbon dioxide. Fill also *one* of the larger cylindrical gas jars, greasing its mouth, and closing it with a glass disc when full.

The following properties of the gas may be examined:—

1. Its pungent, penetrating smell, and the white fumes which it forms in moist air¹ will have been already noticed.

2. Its high density, $1\frac{1}{2}$ times that of air.

3. Its acid reaction on litmus.

4. Its relation to combustion.

These three properties may be tried in one experiment, as follows.

Place a piece of blue litmus-paper at the bottom of a cylindrical gas jar, and support in the jar the taper, lighted, resting the wire against the side of the jar. Pour some hydrogen chloride from one of the bottles into the jar. The taper will be extinguished, and the litmus-paper will be strongly reddened. Observe, however, that the gas does not descend quite so readily as carbon dioxide, showing that the difference between its density and that of air is not quite so great.

5. Its solubility in water.

Fill the supplementary pan of the pneumatic trough (or a deep basin) with water. Take the gas jar which was filled with hydrogen chloride, plunge its mouth (still closed with the glass disc) deeply into the water, and slowly withdraw the disc. The water will rush violently up into the jar, and will fill it entirely if the gas is pure and unmixed with air, showing that hydrogen chloride is extremely soluble in water. Add a few drops of solution of litmus to the liquid in the jar; it will at once be

¹ These are due to its combination with the water-vapour in the air to form a product less volatile than itself, which is therefore condensed into fine liquid drops, forming a mist.

reddened. The hydrogen chloride ('hydrochloric acid') used in the laboratory is simply a strong solution of this gas.

6. Its direct combination with ammonia.

This has been already noticed under AMMONIA: it may now be tried more fully in the following way.



Hyd. Chloride.

Fig. 85.

Place a bottle of the gas on the table, and replace its stopper by a glass plate. Take a similar bottle of ammonia¹, invert it, and replace its stopper quickly by a glass plate. Place the mouths of the bottles close together (fig. 85), the bottle of ammonia being inverted and uppermost, and remove both plates, thus allowing the gases to mix. Dense white clouds will be produced in both bottles (showing that the gases quickly diffuse though they differ greatly in density), and still more if the position of the bottles is reversed, their mouths being still held together, so that the bottle of hydrogen chloride is uppermost, causing the heavier gas to

descend into the lighter. Enough heat is evolved by the union of the gases to make the bottles sensibly warm; and a snow-white powder is deposited in flakes on the sides of the bottles. The two gases, in combining, form a single substance, ammonium chloride, or 'sal ammoniac'².

When the action is over, examine the properties of this salt as follows. Pour 10 c.c. of distilled water into one of the bottles,

¹ If no bottles of ammonia are at hand, pour a little of the *strongest* solution of ammonia into a gas bottle, and shake it up, taking care that the stopper is not blown out. Loosen the stopper for a moment to let air escape, and then shake up the liquid again. In this way enough ammonia gas will be given off to fill the bottle. Lastly, invert the bottle, and loosen the stopper so as to let the liquid escape into a basin or the sink: you may then use the bottle of gas in the above experiment.

²

Hydrogen chloride.		Ammonia.		Ammonium chloride.
HCl	+	H ₃ N	=	H ₄ NCl

shake it up until the white powder is dissolved, then pour the liquid into the other bottle and dissolve the deposit in it also. Place the liquid in a porcelain dish and evaporate it to dryness, using a gentle heat.

(a) Scrape together some of the white residue with a spatula, place it in a test-tube, and heat it over the lamp. It will volatilise entirely, forming a white ring in the cooler part of the tube. This distillation of a solid substance is called 'sublimation.' Observe that the substance does not fuse before volatilising, but passes at once from the solid to the gaseous state. This is an exception to the general rule that solids become liquids before they volatilise.

(b) Dissolve the remainder of the residue in a little water and test the solution with blue litmus and turmeric-paper. No alteration of colour will be produced in either case¹, while we have seen that hydrogen chloride reddened litmus-paper, and that ammonia reddened turmeric-paper. By the combination of the two gases a neutral salt has been formed.

7. Its decomposition by hydrogen nitrate.

The action in this case consists in the combination of the hydrogen of the hydrogen chloride with oxygen yielded by the hydrogen nitrate: chlorine being evolved, which at the moment of its liberation (in the 'nascent state,' as it is termed) acts upon substances with even more than its usual intensity.

Mix about 3 c.c. of strong hydrogen chloride with one-third its volume of strong hydrogen nitrate in a test-tube, and warm gently. The fluid will become yellow, and will give off an orange gas, which is a mixture of chlorine and nitrosyl chloride². Put into the liquid a bit of gold-leaf wrapped round a glass rod: it will be immediately dissolved, forming gold chloride. This mixture of acids is called 'aqua regia' (an old alchemical name), and is much used for dissolving gold, platinum, and some

¹ It may be found *slightly* acid, since the salt is dissociated to a small extent by long boiling with water, traces of ammonia being given off: the residue, therefore, would contain a corresponding amount of free acid.

² $3\text{HCl} + \text{HNO}_3 = 2\text{H}_2\text{O} + \text{NOCl} + \text{Cl}_2$

other substances, which are insoluble in either hydrogen chloride or hydrogen nitrate alone.

8. Its action on metals and metal-oxides, forming chlorides.

(a) On metals, such as iron.

In these cases the metal simply replaces the hydrogen of the acid, which is given off as gas, while a chloride of the metal is formed. This has been already illustrated in the case of zinc, p. 80, and the experiment may be repeated with iron filings: a similar action occurs, and a pale green solution of iron proto-chloride will be formed.

(b) On metal-oxides, such as mercury oxide.

The action of hydrogen chloride on these substances consists in a double decomposition: the hydrogen of the acid changing places with the metal of the oxide, water and a metal chloride being formed.

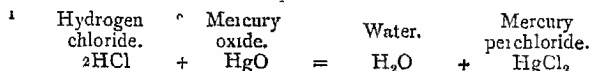
Put a little mercury oxide into a test-tube, and add 3 or 4 c.c. of dilute hydrogen chloride. The oxide will quickly dissolve on shaking and warming the mixture¹: and if the solution is evaporated in a dish to the crystallising point, and left to cool, prismatic crystals of mercury perchloride will be formed.

Properties of Chlorides.

[A solution of sodium chloride containing 0.5 gramm. of the salt in 40 c.c. of water may be used.]

*1. Their solutions, when mixed with silver nitrate, give a white precipitate, soluble in ammonia, but insoluble in hydrogen nitrate.

Put a few drops of the solution of sodium chloride into a test-tube, add 6 or 8 c.c. of water and then a few drops of solution of silver nitrate. A white precipitate of silver chloride will be formed, which, on addition of a little hydrogen nitrate and after thoroughly shaking the mixture, will (if the silver nitrate



is in excess) readily separate in flocks, leaving the liquid almost clear. Pour off the solution, shake up the precipitate with some fresh distilled water, and again pour off the fluid, after allowing the precipitate to subside. Silver chloride is one of the easiest substances to wash thus, by decantation. Divide the precipitate into two parts by shaking it up with a little water and, before it has had time to settle, pouring off one-half of the liquid into another test-tube.

(a) To one portion, after pouring off the water, add some solution of ammonium hydrate, and warm it. The precipitate will readily dissolve, but will be thrown down again on adding dilute hydrogen nitrate to the solution.

(b) To the other portion, after pouring off the water, add a little strong hydrogen nitrate and boil for half a minute. It will remain quite unacted on; a property which distinguishes it from the somewhat similar precipitate formed by a cyanide (Expt. 2 b, p. 226).

***2. When heated with manganese dioxide and hydrogen sulphate, they give off chlorine.**

Pour a few drops of solution of sodium chloride upon a little manganese dioxide in a test-tube and add 2 or 3 c.c. of strong hydrogen sulphate. On warming it gently chlorine will be evolved, which may be recognised by its smell, its colour (best seen by looking across the tube placed against a sheet of white paper), and its action on a slip of wetted litmus-paper held in the tube, which will be first reddened, then bleached.

COMPOUNDS OF CHLORINE WITH OXYGEN.

Chlorine forms a series of compounds with oxygen very analogous to the nitrogen oxides. They are, however, so unstable and explosive that few experiments can easily be made with them. But several important series of salts are known, which contain radicles consisting of chlorine, associated with oxygen. The principal of these are the hypochlorites and chlorates.

23. HYPOCHLORITES.

	Formula of molecule.
[Typical examples,—Potassium hypochlorite,	$K(ClO)$
Calcium hypochlorite,	$Ca(ClO)_2$

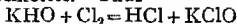
These are compounds related to chlorine monoxide (Cl_2O), which contain a radicle consisting of one atom of chlorine associated with one atom of oxygen. They may be formed by the action of chlorine upon metal-hydrates, or metal-oxides in presence of water.

Preparation of Potassium hypochlorite.

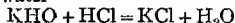
Pour 10 c.c. of solution of potassium hydrate into the bottle of chlorine which was reserved in Ex. 21, put a strip of paper between the stopper and neck of the bottle, and shake the bottle for a minute or so. The chlorine will entirely disappear (but the liquid will not become strongly yellow, as was the case when chlorine dissolved in water, p. 232): it acts upon the potassium hydrate to form two salts, potassium chloride and potassium hypochlorite¹. The peculiar sweetish smell of the solution should be noticed, differing greatly from the strong smell of chlorine itself.

A similar change occurs when calcium hydrate ('slaked lime') is exposed to chlorine for some time: a mixture of calcium hypochlorite and calcium chloride is thus obtained, which is commonly known as 'bleaching powder.'

¹ The action may be explained thus: The molecule of chlorine contains two atoms (Cl_2); one of these takes out the atom of hydrogen from a molecule of potassium hydrate (KHO), forming hydrogen chloride (HCl), while the other atom of chlorine installs itself in the place of the hydrogen, forming potassium hypochlorite. Thus—



This hydrogen chloride in presence of more potassium hydrate forms potassium chloride and water—



The above action of chlorine, in combining with the hydrogen of a compound, and substituting itself, atom for atom, for the displaced hydrogen, is a rather common one: occurring, for instance, when a mixture of methane (H_4C) and chlorine is exposed to light.

Properties of Hypochlorites.

[For the following experiments the solution of potassium hypochlorite, obtained above, may be used. Or a solution of calcium hypochlorite may be made by mixing 50 c.c. of water with 5 grms. of bleaching powder, allowing it to stand for a few minutes (shaking it occasionally but not heating it), and filtering from the residue of lime which is sure to remain.]

1. They give up oxygen readily.

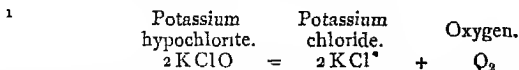
(a) Put about 5 c.c. of the solution of potassium hypochlorite into a test-tube, add one drop of solution of cobalt nitrate (which will produce a black precipitate of cobalt peroxide) and warm the mixture gradually. Oxygen will be given off with effervescence, and may be tested for by a glowing splinter of wood in the usual way¹. The cobalt oxide is not altered, at any rate not permanently so; it seems to act in the same way as the manganese dioxide in the usual method of preparing oxygen, p. 115.

This reaction has been proposed as a practical method of obtaining oxygen.

*(b) Add a few drops of the solution of potassium hypochlorite to a little solution of lead acetate in a test-tube, and warm the mixture. The white precipitate at first formed, containing lead protoxide, soon turns brown; the lead combining with more oxygen to form lead dioxide.

*2. When acted on by hydrogen chloride, they yield chlorine.

Place a little bleaching powder at the bottom of a small test-tube, and pour on it a few drops of strong hydrogen chloride. A violent action will take place, and a greenish yellow gas will fill the tube, which may be proved to be chlorine by its odour and bleaching action on litmus-paper².



² The reaction is interesting as affording evidence that the molecule of chlorine is made up of two chlorine-atoms. Hydrogen hypochlorite is first formed by double decomposition; and then a molecule of chlorine is

In the case of ordinary bleaching powder, any acid will produce the same effect as hydrogen chloride; since the substance contains calcium chloride as well as calcium hypochlorite; and the calcium chloride yields hydrogen chloride when decomposed by an acid.

3. They bleach organic colouring matters, but only when a free acid is present.

(a) Dip a piece of blue litmus-paper into the solution of potassium hypochlorite. Its colour will not be altered. Lay it on a plate and pour on it a drop or two of dilute hydrogen sulphate; it will be immediately bleached. The reason is that hydrogen hypochlorite is formed by the action of the acid, and this is much less stable than the potassium hypochlorite, and gives up its oxygen to the colouring matter, forming a colourless compound.

(b) Place a little solution of bleaching powder in a small beaker, and add to the liquid a drop or two of solution of blue litmus. The colour of the litmus will remain unchanged. Now blow air from the mouth into the solution through an elbow tube. The blue colour will soon disappear; the carbon dioxide of the breath having, in presence of water, decomposed the calcium hypochlorite in the same way as the hydrogen sulphate in the previous experiment.

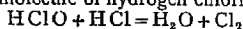
(c) Add a few drops of solution of potassium hypochlorite to a dilute solution of indigo sulphate (which always contains free acid). The blue colour will be at once discharged.

4. They decompose and destroy many injurious products of putrefaction.

This property is due to the facility with which hypochlorites yield both chlorine and oxygen in a 'nascent' state, and it has led to their extensive use for disinfecting purposes. The use of bleaching powder as a disinfectant may be thus illustrated—

Place a few drops of solution of hydrogen sulphide (which is

formed by the union of one atom derived from the hydrogen hypochlorite and one atom from the molecule of hydrogen chloride. Thus—



one of the poisonous gases given off in sewers) in a test-tube, add a small quantity of bleaching powder and shake the mixture. Observe that the offensive smell of the gas entirely disappears; the hydrogen sulphide has, in fact, been decomposed by the oxygen yielded by the calcium hypochlorite, with formation of water and sulphur¹.

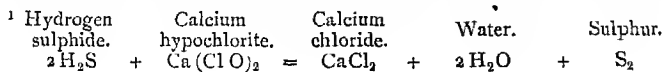
Additional Experiment.

Use of hypochlorites in calico-printing.

It is clear from the above experiments that white patterns may be formed on coloured cloth by putting an acid on certain parts of it, and then dipping it into a solution of a hypochlorite, which will only discharge the colour where it meets with the acid. This is the principle of the 'discharge' process of dyeing, and may be illustrated as follows.

Dissolve 3 grms. of hydrogen tartrate (tartaric acid) in 10 c.c. of water: heat the solution to boiling and add by degrees half a gramme of starch previously shaken up with 5 c.c. of cold water. Boil the mixture cautiously, stirring and shaking it, until it becomes rather viscid (the object of adding the starch is to prevent the solution from spreading over the material to which it is applied; solution of gum arabic may be substituted, if at hand).

Take a small piece of coloured cloth or calico (the thin cotton cloth dyed with madder answers well), lay it flat on a double fold of blotting paper, and draw on it letters with a glass rod dipped in the acid solution, taking care that the liquid thoroughly penetrates the cloth, but does not spread much laterally. Dry this partially before a fire or by laying it on wire-gauze at some distance above a small lamp-flame, and meanwhile make a strong solution of bleaching powder by grinding about 20 grms. of it with enough water to make a thin cream, then rinsing it into a flask, adding about 100 c.c. of water, and shaking it up thoroughly. Lastly, it must be filtered from the residue, mainly of calcium hydrate, which is sure to remain. Warm the filtered solution slightly, and pour it upon the piece of coloured cloth laid flat on a plate, taking care to soak the whole of the cloth in the liquid, and



seeing that it is kept flat and that no folds overlies each other. The acid will at once decompose the calcium hypochlorite: chlorine will be liberated, as above explained, and will discharge the colour in those parts where the acid was placed. As soon as the design appears in white, remove the cloth from the solution, and rinse it well in plain water.

24. CHLORATES.

Formula of
molecule.

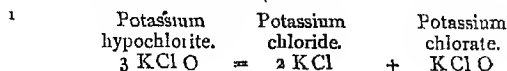
[Typical example,—Potassium chlorate, $K(ClO_3)$]

These are salts related to chlorine pentoxide (Cl_2O_5), which contain a radicle consisting of one atom of chlorine associated with three atoms of oxygen. They are formed when solutions of hypochlorites are heated to boiling; a part of the salt giving up oxygen to the rest, and being itself reduced to a chloride.

Preparation of Potassium chlorate.

Take the solution of potassium hypochlorite which was obtained in Ex. 21, p. 231, by saturating potassium hydrate with chlorine, and evaporate it down in a dish until a drop placed on a watch glass deposits crystals on cooling; then leave it to crystallise.

In this reaction two molecules of the potassium hypochlorite give up all their oxygen to a third molecule, which is thus converted into potassium chlorate¹. Thus the liquid contains a mixture of potassium chlorate and potassium chloride; and the former being much less soluble in water than the latter, crystallises out in the form of flat rhombic plates as the solution cools. These may be drained from the liquid, washed with a little water, and left to dry in a funnel. The liquid drained from the crystals will contain much potassium chloride, as may be proved by testing it with silver nitrate. The crystals should be proved to be a chlorate by tests 2 and 4.



Properties of Chlorates.

[For some of the following experiments a solution of potassium chlorate will be required, containing 1 grm. of the salt dissolved in 40 c.c. of water.]

***1. When heated, they readily give up oxygen.**

A proof of this has already been given in the first experiment made in the preparation of oxygen, p. 114.

Put a small crystal of potassium chlorate into an ignition-tube, add a splinter of charcoal, and heat nearly to redness. A deflagration will be observed similar to that which took place in the corresponding experiment with nitrates, p. 163, the potassium chlorate giving up all its oxygen to the carbon, with formation of potassium chloride and carbon dioxide.

***2. When acted on by hydrogen sulphate, they yield a deep yellow gas, chlorine tetroxide.**

Powder a *very small* fragment of potassium chlorate (not larger than a grain of wheat); put it into a test-tube, and pour on it two or three drops of strong hydrogen sulphate. The mixture will turn yellow or orange, and a deep yellowish-green gas (chlorine tetroxide)^f will be given off, having a very characteristic smell, somewhat resembling (but easily distinguishable from) that of chlorine.

***3. When heated with indigo sulphate, they destroy its blue colour.**

Make a strongly-acid, dilute solution of indigo sulphate precisely as directed under NITRATES (expt. 2, p. 163): heat it to boiling and add one or two drops of solution of potassium chlorate. The blue colour of the indigo will be destroyed, as in the case of nitrates, and for the same reason, *viz.* the oxidation of the colouring matter.

***4. When mixed with hydrogen sulphite, they bleach indigo at once, without being heated.**

This action depends upon the reduction of chlorates by hydrogen sulphite, which has a great tendency to absorb oxygen (as will be explained under SULPHITES p. 283): lower and less

stable compounds of chlorine are formed, which readily give up chlorine, decomposing the indigo.

Add a drop of solution of indigo sulphate to some solution of potassium chlorate. Put into another test-tube some dilute solution of hydrogen sulphite (or, if this is not at hand, of sodium sulphite, to which a few drops of hydrogen sulphate have been added; hydrogen sulphite is thus formed by double decomposition), and add to it also a drop of indigo sulphate. In neither case will the blue colour be discharged at once. Now mix the contents of the two tubes; the blue colour of both the solutions will disappear, for the reason above explained.

[This reaction serves to distinguish a chlorate from a nitrate, since the latter will not under the same conditions bleach indigo at once. The experiment should be repeated, using a solution of potassium nitrate instead of potassium chlorate, to prove this fact.]

5. Their solutions, when tested with silver nitrate, give no precipitate.

Add a drop of solution of silver nitrate to some of the solution of potassium chlorate. No precipitate will be produced if the chlorate is pure, since silver chlorate (as indeed every other chlorate) is soluble in water¹.

Observe that although chlorine is present in the chlorate, it is present in such a condition as to be unable to combine *per se* with silver to form a chloride.

Additional Experiments.

Preparation of Chlorine tetroxide.

[Formula of molecule, Cl_2O_4

Weight „ 135 hydrogen atoms.]

This is the only one of the chlorine oxides with which experiments can be at all safely made. It is obtained by the action of hydrogen sulphate upon a chlorate, such as potassium chlorate.

¹ Commercial potassium chlorate generally contains a trace of chloride, sufficient to give a turbidity with silver nitrate, but it may be readily purified by dissolving in as little hot water as possible (about 20 grms. in 60 c.c.) and re-crystallising.

[Do not, on any account, take larger quantities of the substances than those indicated below.]

Put 2 c.c. of strong hydrogen sulphate into a test-tube, add *very gradually* half a gramme (not more) of potassium chlorate, coarsely powdered, and place the tube in a beaker containing warm water (not hotter than 40°C .; 30 c.c. of cold water mixed with the same volume of boiling water will be hot enough). The mixture will become deep orange and give off chlorine tetroxide with effervescence¹.

The action may be allowed to go on until the gas, which has a high density, has nearly filled the tube; the latter should then be taken out of the warm water and supported in an empty gas bottle or beaker, in a draught-cupboard.

Properties of Chlorine tetroxide.

1. Its intense yellow colour and characteristic smell will have been noticed already.

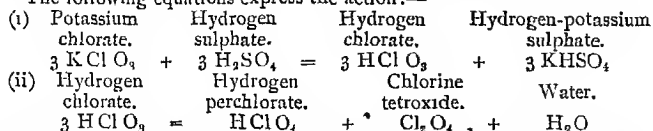
2. Its sudden decomposition when slightly heated.

Take a piece of wire bent at right angles (the wire to which the taper is affixed, fig. 12, p. 8, the taper being removed, will do very well), heat one end of it slightly in a lamp-flame, and plunge it while hot into the gas in the test-tube. The gas will decompose, with a slight explosion, into chlorine and oxygen; the greenish yellow colour almost entirely disappearing, since the colour of the chlorine produced is far less intense.

3. Its decomposition by oxidisable bodies, such as phosphorus.

Nearly fill a large wine-glass or beaker with water, and drop into it a few crystals of potassium chlorate, which will sink to the bottom without much loss, as the salt is not very soluble in water. Drop upon the crystals a bit of phosphorus about half as large as a pea, and support a tube funnel in the glass in such a position that the extremity of the tube may just touch the crystals at the bottom of

¹ The following equations express the action:—



It will be seen that the hydrogen chlorate is split up into a higher and a lower oxygen-compound of chlorine. Compare the decomposition of a hypochlorite into a chlorate and chloride.

the glass. Now pour down the funnel 2 or 3 c.c. of strong hydrogen sulphate; chlorine tetroxide will be evolved when the acid comes in contact with the potassium chlorate, and the phosphorus will take fire, as in chlorine gas, and burn underneath the water.

[When the experiments are over, pour the mixture in the tube and beaker into a jug of water at once, and throw it away: the tube may then be safely washed out with water.]

25. BROMINE.

[Symbol of atom,	Br
Weight ,,	80 hydrogen-atoms.
Formula of molecule,	Br ₂
Weight ,,	160 hydrogen-atoms.]

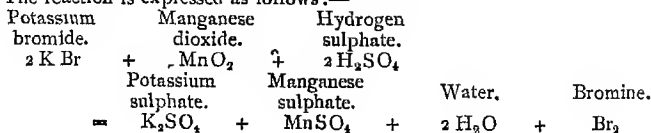
Preparation of Bromine.

[The vapour of bromine is even more offensive in smell and poisonous than that of chlorine, and all possible precautions should be taken not to inhale any of it: all experiments being done in a draught-cupboard.]

This element, which occurs in combination as sodium bromide and magnesium bromide in sea water and certain mineral springs, is obtained from sodium bromide or potassium bromide by a reaction precisely analogous to that by which chlorine was obtained from sodium chloride (p. 230).

Mix intimately in a mortar about half a gramme of potassium bromide with twice as much manganese dioxide. Put the mixture into a dry test-tube, add about 3 c.c. of strong hydrogen sulphate, and heat the tube very gently on a sandbath placed in a draught-cupboard, supporting it upright by passing over it the smallest retort ring, and placing behind it a sheet of white paper. Deep red vapours of bromine will soon fill the tube, and will condense near the top into an intensely red liquid¹.

¹ The reaction is expressed as follows:—



Properties of Bromine.

1. Its deep red colour and offensive smell will have been already noticed.

2. Its action on litmus.

Dip a wetted piece of blue litmus-paper into the vapour. It will be at once bleached.

3. Its high density, and solubility in water.

Put about 5 or 6 c.c. of water into a test-tube, and pour on it some bromine by inclining the tube containing the vapour (taking care that none of the mixture in the tube is poured out as well). The vapour will readily be transferred in this way, showing its high density. Now shake up the water with the bromine vapour, closing the mouth of the tube with the finger. An orange-coloured solution of bromine will be readily formed.

4. Its bleaching action on indigo.

Pour one or two drops of the solution of bromine just obtained into a dilute solution of indigo sulphate (two drops in 10 c.c. of water): the blue colour will be at once discharged, as in the case of chlorine.

[Keep the rest of the solution of bromine for the next experiment.]

26. BROMIDES.

Formula of
molecule.

[Typical examples,—Potassium bromide, KBr
Hydrogen bromide, HBr
• Silver bromide, AgBr]

Formation of Potassium bromide.

Add a few drops of solution of potassium hydrate to the solution of bromine just obtained. The orange colour will disappear, the bromine uniting with potassium and oxygen to form at first potassium hypobromite (KBrO), but eventually a mixture of

potassium bromide and potassium bromate¹. This result is analogous to that which takes place when chlorine acts upon potassium hydrate and the potassium hypochlorite thus formed is heated to boiling (p. 246); but in the case of bromine the potassium hypobromite is soon decomposed even in the cold.

In practice, to get rid of the bromate, the above mixture is gently ignited; the potassium bromate gives off its oxygen (like chlorates, p. 247), and pure potassium bromide remains.

Properties of Bromides.

[Crystallised potassium bromide, and a solution of it containing 1 grm. dissolved in 40 c.c. of water may be used.]

1. When mixed with hydrogen sulphate they are decomposed, yielding hydrogen bromide mixed with vapours of bromine.

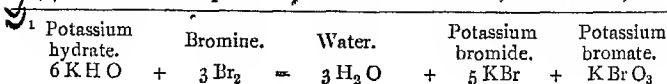
Place a little powdered potassium bromide in a test-tube and add a few drops of hydrogen sulphate. A strong action takes place, and a gas forming white fumes in moist air is given off, which is hydrogen bromide; but this is itself partly decomposed by hydrogen sulphate, orange vapours of bromine being set free. Hence hydrogen bromide cannot be obtained pure by the same method as hydrogen chloride: it is usually prepared by a process of which the principle will be explained under IODIDES.

*2. When tested with silver nitrate they give a yellowish-white precipitate, insoluble in hydrogen nitrate, but difficultly soluble in ammonia.

Add a drop of solution of silver nitrate to solution of potassium bromide. A yellowish-white precipitate of silver bromide will be formed. Divide the liquid in which the precipitate is suspended into two parts;

(a) add to the one some hydrogen nitrate; the precipitate will not dissolve.

(b) To the other portion add some ammonia, and warm; the



precipitate will dissolve by degrees, but not so readily as silver chloride. The fact of its solubility may be proved, without waiting until all the precipitate has disappeared, by pouring off a little of the clear liquid into another tube and adding to it some dilute hydrogen nitrate: the portion of silver bromide which had dissolved will be again precipitated.

*3. They are decomposed by chlorine, with liberation of bromine.

Add a few drops of solution of chlorine to some solution of potassium bromide in a test-tube. The bromine will be displaced by the chlorine from its combination with potassium, and will dissolve in the excess of potassium bromide, colouring the solution yellow.

Now add a small quantity of carbon disulphide¹, close the tube with the thumb and shake the mixture thoroughly; then allow it to stand for a few moments in order that the scattered particles of the carbon disulphide may collect at the bottom of the tube in one globule, which will be found to have acquired an orange tint, while the fluid above it will be colourless. The bromine has been withdrawn entirely from the solution by the carbon disulphide, in which it is very soluble. Pour off most of the upper stratum of fluid, fill up the test-tube with water, and again pour it off; then add some solution of potassium hydrate, shake it up, and allow it to stand as before. The globule of carbon disulphide will be found to have lost its colour, the bromine having acted upon the potassium hydrate, to form potassium bromide and bromate, as just now explained.

27. IODINE.

[Symbol of atom,	I
Weight ,,	127 hydrogen-atoms.
Formula of molecule,	I ₂
Weight ,,	254 hydrogen-atoms.]

The main source of iodine is 'kelp,' which is the stony ash

¹ If carbon disulphide is not at hand, ether will serve the purpose, as it will form a coloured stratum on the top of the aqueous solution.

remaining when sea-weeds are burnt; sea-plants having a remarkable power of absorbing the traces of iodides which exist in the water. Iodine has many striking analogies to chlorine and bromine, but it is a solid at ordinary temperatures, and its vapour when formed is not so injurious and unpleasant as the other two elements. Hence it will be unnecessary to take the same precautions in experimenting upon it.

Preparation of Iodine.

The element is usually obtained from potassium iodide by a reaction similar to that by which chlorine and bromine are prepared.

Weigh out 3 grms. of potassium iodide and the same quantity of manganese dioxide, mix them intimately in a mortar and put the mixture into a porcelain dish about 8 or 9 cm. in diameter; then add 5 c.c. of strong hydrogen sulphate, stir the whole thoroughly together, and cover the dish with an inverted funnel just large enough to fit within the rim. The outside of the funnel should be covered with slips of blotting paper kept moist with water, to ensure complete condensation of the vapours, and the end of the tube should be stopp'd with a plug of cork. Place the dish on a sandbath and heat it gently. Deep violet vapours of iodine will be formed, and will condense in the upper part of the funnel in glittering rhombic plates, the crystalline form of which may easily be made out with a magnifying-glass¹. In a few minutes sufficient iodine will be obtained for use in the following experiments.

Properties of Iodine.

[It should be borne in mind that iodine stains the skin yellow, and therefore it should be handled as little as possible. A glass rod or platinum (not aluminium or bone) spatula should be used. Stains may be removed by dilute solution of ammonium hydrate.]

¹ Very fine crystals of iodine are often formed by spontaneous sublimation on the stopper of a bottle containing it.

***1. It melts and volatilises readily, forming a violet vapour, much heavier than air.**

Put a few crystals of iodine into a large dry test-tube, and heat them gently. They melt into an almost black liquid, and on further heating turn into a splendid violet vapour. Warm the upper part of the tube (held in a paper holder, fig. 58, p. 68), to prevent the condensation of the vapour, and when the tube is full of it pour some out on a white plate. The heavy vapour will pour out almost like a liquid, and will condense into a cloud of small flakes of iodine which will fall in a shower on the plate.

2. It is scarcely soluble in water.

Place a crystal or two of iodine in a test-tube, pour on them about 5 or 6 c.c. of water, and shake the mixture. Hardly any of the substance will dissolve; only sufficient to colour the liquid a pale yellow.

3. It readily dissolves in alcohol.

Pour off the liquid from the crystals used in the last experiment, and add to them 2 or 3 c.c. of alcohol. A red solution will be at once formed, rapidly deepening in colour, when the tube is shaken, until it becomes almost opaque. Now fill up the tube with water; most of the iodine will be reprecipitated as a black powder.

4. It also dissolves in solution of potassium iodide.

Put about half a gramme of crystallised potassium iodide into a test-tube, add 5 or 6 c.c. of water and then a few crystals of iodine. The latter will dissolve even more readily than in alcohol; but it will not be reprecipitated on filling up the tube with water.

[Use the solution in the following experiments.]

***5. It forms a deep blue compound with starch.**

This is the most characteristic and delicate test for iodine, when it is free and uncombined: mere traces of it being recognisable.

Pour five or six drops only of the solution of iodine obtained

in the last experiment into a beaker, add 100 c.c. of water and then 8 or 10 c.c. of a *freshly-made* solution of starch¹. A deep blue colour will be produced, even in so highly dilute a solution of iodine.

Pour a little of the liquid into a test-tube, add a drop or two more of the solution of iodine, to deepen the colour, then heat it over a lamp. When it has nearly reached the boiling point the blue colour will quickly disappear, showing that the compound of iodine with starch is decomposed by heat. Cool the liquid by holding the tube in a stream of water (or in a jug of cold water); the blue colour will soon reappear and become as intense as at first². Hence in testing for iodine by this method care must be taken that the liquid is quite cold.

[Conversely, iodine may be used as a test for starch. If a few drops of a very dilute solution of iodine, acidified with hydrogen acetate, are put on a piece of writing paper, a blue colour will be produced on account of the starch present in the size used in making the paper. Similarly, a slice of raw potato may be shown to contain starch.]

6. It decomposes hydrogen sulphide.

This is due to its affinity for hydrogen, in which property it resembles chlorine.

Add a little solution of hydrogen sulphide to the rest of the solution of iodine in potassium iodide obtained in expt. 4. The orange colour of the liquid will disappear, and a slight milky deposit of sulphur will be formed. The iodine has, in fact, combined with the hydrogen, forming hydrogen iodide, and left the sulphur, for which it has little affinity³.

This reaction is often used to prepare a solution of hydrogen iodide: iodine being shaken up with water, and a current of hydrogen sulphide passed through it.

¹ For the method of making this see Appendix B.

² Notice that the blue colour reappears first in the *lowest* part of the liquid. It reappears, of course, where the liquid is coldest; and the fact that it appears at the bottom is a proof that cold water is denser than hot water.

³

Iodine.		Hydrogen		Hydrogen		Sulphur.
2 I_2	+	sulphide.	=	iodide.	+	S_2
		$2 \text{ H}_2\text{S}$		4 HI		

28. IODIDES.

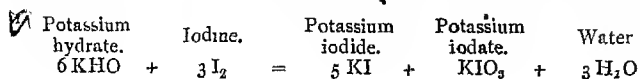
	Formula of molecule.
[Typical examples,—Hydrogen iodide,	HI
Potassium iodide,	KI
Silver iodide,	AgI
Phosphorus tri-iodide, PI_3]	

The formation of one or two of these compounds of iodine with other radicles has been illustrated already. Thus iodine was shown to combine readily with phosphorus and with mercury (pp. 81, 82).

Preparation of Potassium iodide.

Iodine acts precisely like bromine (and not altogether like chlorine) upon metal-hydrates; a mixture of iodide and iodate being at once formed, without any intermediate product such as hypo-iodite.

Put 5 c.c. of solution of potassium hydrate into a test-tube, and add iodine little by little, shaking the mixture constantly, as long as it is dissolved. A very slight excess should be added; just enough to give the liquid an orange-yellow colour (if too much is inadvertently put in, a drop or two of potassium hydrate may be added). A mixture of potassium iodide and potassium iodate is thus obtained¹, which should be evaporated to dryness in a small dish. In order to obtain pure potassium iodide, the residue must be heated to low redness in the dish, when the potassium iodate will be decomposed (precisely like potassium chlorate) into oxygen and potassium iodide. Continue the heat until the mass ceases to effervesce, melting quietly in the dish; then leave it to cool on sand or wire-gauze. The residue may be dissolved in a little water and its purity tested by pouring a few drops into a test-tube, diluting with water and adding a little



dilute hydrogen sulphate. If any traces of iodate remain undecomposed, iodine will be set free, colouring the "solution yellow". If found pure, it may be used in the following experiments.

Properties of Iodides.

[A solution of potassium iodide containing 1 grm. of the pure colourless salt ² dissolved in 30 c.c. of water may be used.]

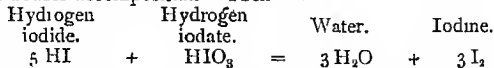
***1. When mixed with strong hydrogen sulphate, they are (as a rule) decomposed, yielding hydrogen iodide and iodine.**

Place a little powdered potassium iodide in a test-tube, pour on it a few drops of strong hydrogen sulphate, and warm gently. Hydrogen iodide will be evolved with effervescence, forming white fumes in moist air (like hydrogen chloride); but it will be mixed with violet vapours of iodine. It is, in fact, partly decomposed by the excess of hydrogen sulphate as explained below ³.

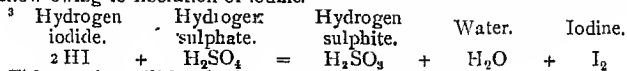
***2. When mixed with silver nitrate, their solutions give a pale yellow precipitate of silver iodide, insoluble in ammonia.**

Pour a few drops of the solution of potassium iodide into a test-tube, dilute with water, and add one or two drops of solution of silver nitrate. A yellow precipitate of silver iodide will form in the liquid, which should be divided into two portions.

¹ The formation of iodine here is due to one of those remarkable actions in which a molecule is built up of two atoms taken from different sources (compare the action between hydrogen chloride and hydrogen hypochlorite, p. 243, note). Hydrogen iodide and hydrogen iodate are first produced by the usual double decomposition. Then—



² Potassium iodide is very apt to decompose on keeping, especially if exposed to the light, or if it contains any potassium iodate, becoming yellow owing to liberation of iodine.



This reaction will be alluded to again under SULPHITES.

(a) To the one add some strong hydrogen nitrate, which will fail to dissolve it.

(b) To the other add excess of ammonia, which will also fail to dissolve it; as may be proved by allowing it to subside, pouring off some of the clear liquid, and adding to this some dilute hydrogen nitrate, which will produce no precipitate.

***3. They are decomposed by many oxidising agents, with liberation of iodine.**

(a) **By chlorine.**

Add one drop of solution of chlorine to a very dilute solution of potassium iodide (about three drops of the solution to 10 c.c. of water). Iodine will be liberated and will colour the solution yellow. On addition of 2 or 3 c.c. of solution of starch, the characteristic deep blue compound will be formed.

[If a considerable excess of solution of chlorine is now added, the blue colour will disappear, owing to the formation of a colourless iodine chloride which does not act upon starch. Hence in applying this test it is important not to use an excess of chlorine. It is, in fact, best not to use chlorine at all for the purpose of liberating iodine, but hydrogen nitrite, as described in the next experiment.]

(b) **By nitrites.**

Add a few drops of dilute hydrogen sulphate to a very dilute (see last experiment) solution of potassium iodide, and then a drop of a recently-made solution of potassium nitrite. This will decompose the hydrogen iodide formed by the action of the hydrogen sulphate, and liberate iodine (see p. 169). Shake up the yellow solution with a drop or two of carbon disulphide, and allow it to stand for a minute. The carbon disulphide will be found to have withdrawn the iodine from the solution, collecting into a deep purple globule at the bottom of the tube.

[It will be well to repeat the similar experiment with potassium bromide, given on p. 253, and compare the colours of the two globules, the bromine imparting a bright orange, the iodine a fine purple colour to the carbon disulphide. Notice also that potassium nitrite will not decompose hydrogen bromide, but that solution of chlorine must be used for the purpose. If an excess of strong

solution of chlorine is added to the contents of both tubes, and the mixture shaken and again allowed to settle, the globule containing iodine will be found to have lost its colour, while the globule containing bromine remains unchanged.]

Additional Experiments.

Preparation of Hydrogen iodide.

Apparatus required—Large test-tube; corks; cork-borers; elbow-tubes as used in Ex. 12, p. 188; aigand burner, Bunsen's holder; wooden blocks; one large, and three small gas bottles; two cylindrical gas jars, 20×5 cm.; large beaker; glass disc; taper on wire.

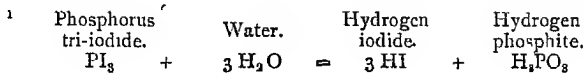
Red phosphorus; iodine; litmus-paper; bleaching powder; strong hydrogen chloride.

[It has been shown already in expt. 1, p. 258, that hydrogen iodide cannot be obtained in a pure condition by a reaction analogous to that by which hydrogen chloride was obtained, *viz.* by decomposing potassium iodide by strong hydrogen sulphate; since part of the hydrogen iodide is itself decomposed by the hydrogen sulphate, and iodine set free.

Hence to prepare the gas recourse is usually had to the action of water on phosphorus tri-iodide. This is of the following nature—the iodine combines with half the hydrogen in three molecules of water, while the phosphorus together with the rest of the hydrogen and the oxygen form hydrogen phosphite (phosphorous acid)¹.

It has been already seen (p. 81) that phosphorus unites readily with iodine, but with a violence which is not easy to control. Hence it is best to use the modification of phosphorus called 'red' or 'amorphous' phosphorus, the affinities of which are much less strong than those of ordinary phosphorus. In any case, however, the process requires care; and strict attention must be paid to the directions given.

Take a large test-tube, about 2.5 cm. in diameter and 16 or 18 cm. in length; adapt to it a cork fitted with an elbow tube and right-angled delivery tube connected by a cork joint, such as was used in the preparation of carbon dioxide, p. 188, and support it in an inclined position in a Bunsen's holder as shown in fig. 86.



Weigh out half a gramme of red phosphorus in powder¹, and transfer it to the test-tube. Pour upon it 1 c.c. (not more) of water, and then (having previously placed a beaker of cold water within reach) add 6 grms. of iodine, and mix the whole by shaking the tube, cooling it as soon as the action begins by dipping it into the beaker of water. The iodine acts on the phosphorus readily but not violently if the temperature is kept down, and the water decomposes the phosphorus tri-iodide, as above explained. We thus obtain a very strong solution of hydrogen iodide, from which the gas will be given off abundantly when it is very gently heated.

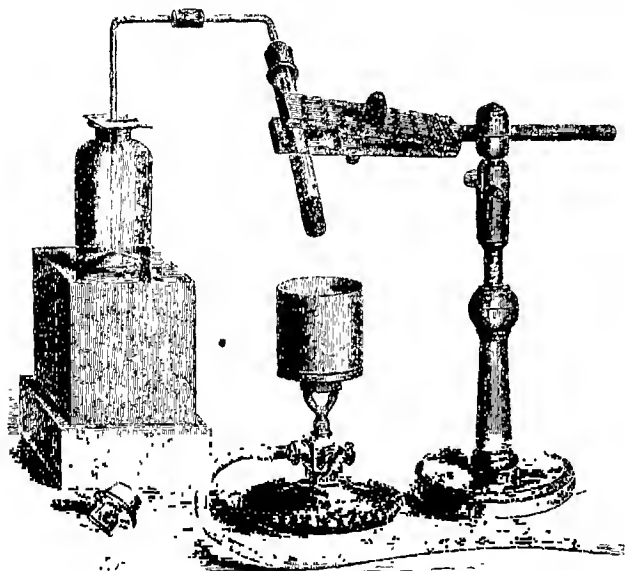


Fig. 86.

Replace the cork with delivery tube, and re-adjust the apparatus in the holder, placing under the end of the delivery tube a small gas bottle covered with a card having a notch cut in it (fig. 82, p. 189).

¹ It is usually sold in a state of powder. If, however, you have obtained it in lumps, it must be ground with care to a coarse powder in a mortar, covering it with water while crushing it with the pestle, in case any small particles of ordinary phosphorus may be present which might inflame by the friction and set the whole mass on fire; then pour off the water and transfer the moist powder to the test-tube.

Now heat the mixture in the test-tube very carefully with a lamp; the gas will soon begin to pass over into the bottle, and from its very high density ($4\frac{1}{2}$ times that of air) it may most readily be collected by downward displacement, its position in the bottle being tested, as in the case of hydrogen chloride, by a lighted taper. Three small bottles and one cylindrical gas jar should be filled with the gas, the flame of the lamp being very slightly raised if the evolution of gas becomes slow.

The unstable nature of the gas will be at once noticed; a slight deposit of iodine will be found in the bottles, even if kept only for a short time; and vapours of iodine will be seen whenever the lighted taper is immersed in the gas.

In most other respects hydrogen iodide strongly resembles hydrogen chloride, and the following properties of the gas may be examined in exactly the same manner as the corresponding properties of hydrogen chloride described in Ex. 22, p. 237, which should be referred to for the details of the experiments.

1. Its pungent smell and the white fumes it produces in moist air.
2. Its extremely high density, $4\frac{1}{2}$ times that of air.
3. Its acid reaction on litmus¹.
4. Its relation to combustion.
5. Its solubility in water.
6. Its decomposition by chlorine.

This reaction serves to distinguish it from hydrogen chloride, and also illustrates well the relative affinities of chlorine and iodine for hydrogen.

Place a large wide-mouthed gas bottle on a sheet of white paper before you. Pour into the bottle a little hydrogen iodide from one of the small bottles, then make a little chlorine by pouring a few drops of strong hydrogen chloride upon a little bleaching powder in a test-tube, and pour some of the gas (by inclining the tube) into the large bottle containing the hydrogen iodide. Violet clouds of iodine will be formed when the gases mix; the chlorine, from its stronger affinity, combining with the hydrogen and liberating iodine.

[After the experiment, wash out the test-tube containing the chlorine with plenty of water, that the gas may not escape unnecessarily into the room.]

¹ It will be noticed that a brown deposit of iodine is formed on the litmus and that the colour of the latter is eventually destroyed, although iodine has by no means the same strong bleaching powers as chlorine and bromine.

The relative affinities of chlorine, bromine, and iodine, respectively, for other radicles.

These three elements form an unusually well defined natural group. A regular gradation of properties exists between them, bromine always occupying the middle place; as shown by their colours, their freezing and boiling points, the weights of their atoms, their affinities for hydrogen, &c., for a fuller account of which analogies a theoretical text-book must be consulted.

1. As a general rule, chlorine shows the strongest chemical power, and iodine the weakest. The bleaching effects of chlorine (expt. 4, p. 232), the violence with which it combines with hydrogen (expt. 8, p. 233), and the fact that it displaces both bromine (expt. 3, p. 253) and iodine (expt. 3, p. 259) from most of their compounds, are proofs of this. The following experiments may serve to illustrate the relative displacement-powers of the three elements.

(a) Put a few drops of solution of potassium bromide into a test-tube, dilute with about 5 c.c. of water and add a few drops of solution of chlorine. Bromine will be liberated, showing that chlorine has a stronger affinity for potassium than bromine has.

(b) Add to the above solution a few drops of carbon disulphide, shake up, and allow the globule to subside. Fill up the test-tube with water, and wash the globule by decantation with three or four changes of water, to free it from all traces of chlorine. Add to the washed globule containing bromine 4 or 5 c.c. of solution of potassium iodide and shake it up. The orange colour of the globule will rapidly change to violet, and if a little solution of starch is added and the mixture again shaken, the blue compound characteristic of iodine will be observed. This proves that bromine has a stronger affinity for potassium than iodine has.

2. It must, however, be observed that this displacement-power depends very much upon the radicles with which the chlorine, bromine, and iodine are associated, and the conditions under which the action takes place. The following experiment will show that, under some circumstances, bromine can displace chlorine, and iodine can displace bromine.

Put eight or ten drops of solution of ammonium chloride into a test-tube, dilute with 3 or 4 c.c. of water and add about two drops (not more) of solution of silver nitrate. A white precipitate of silver chloride will, of course, be formed. Add to this, little by little,

solution of ammonium carbonate, shaking the mixture after each addition, until the precipitate is just re-dissolved. The solution now contains a compound of chlorine with silver and ammonium.

(a) Add to the solution a few drops of solution of potassium bromide¹. A yellowish-white precipitate of silver bromide will be formed. Thus bromine has displaced chlorine from its combination with silver.

Add to the mixture solution of ammonium hydrate until the precipitate is just re-dissolved. The solution now contains a compound of bromine with silver and ammonium.

(b) Add to this solution a few drops of solution of potassium iodide. A yellow precipitate will be formed, easily recognisable as silver iodide. Thus the iodine has been able to displace the bromine and unite with the silver.

29. FLUORIDES.

	Formula of molecule.
[Typical examples,—Calcium fluoride,	Ca F_2
Hydrogen fluoride, HF]	

This is the first element of those dealt with in this book which the student cannot examine in the free condition; indeed, its chemical affinities are so intense that until lately all attempts to isolate it only resulted in its transference from one combination to another. It has now, however, been obtained, though with great difficulty, and is found to be a gas having many points of similarity to chlorine; as was long ago predicted from the close analogy between many of its compounds and those of chlorine.

Its chief natural source is the mineral 'fluor spar' (calcium fluoride), from which its only other highly important compound, hydrogen fluoride ('hydrofluoric acid'), is easily obtained by the action of strong hydrogen sulphate (compare the reaction by which hydrogen chloride is obtained from sodium chloride, p. 230).

¹ Solution of bromine will answer as well, if at hand.

Preparation of Hydrogen fluoride, and its action upon glass.

Hydrogen fluoride has a remarkable power of decomposing and dissolving glass and other silicates, owing to its affinity for the silicon they contain. Hence it is extensively used for engraving and etching glass, as in forming graduations on thermometers, labels on bottles, patterns on lamp glasses, &c.

* Take a small cup of lead or platinum (a leaden ink-well answers perfectly)¹ and put into it as much powdered fluor spar as will lie on the end of a spatula. Obtain a piece of sheet glass about 6 cm. square, lay it on wire-gauze and warm it gently over a lamp-flame. When it is fairly hot, rub over its surface a piece of beeswax (or wax candle) wrapped in a bit of calico, so that the wax as it melts may filter through the calico and form an even layer upon the plate. Set it up edgeways to cool, on a piece of paper, and then place it with the coated side upwards on the table, and trace on it with a pointed piece of wood (a match cut like a pencil answers very well) any letters or device which may occur to you, taking care that the lines are drawn quite through the wax so as to expose the bare glass. Pour enough strong hydrogen sulphate upon the fluor spar in the leaden dish to make a thin paste, mix the two thoroughly by stirring with a glass rod (which should be washed immediately afterwards) and cover the dish with the piece of glass, the coated side being downwards. Heat the dish very gently by placing it on some warm sand, and leave it for a short time undisturbed, taking especial care not to use so much heat as to melt the wax. The hydrogen sulphate will decompose the fluor spar, forming calcium sulphate, while gaseous hydrogen fluoride will be evolved², which will act upon the glass where it

¹ A cup of lead may be made by turning up the edges of a circular piece of thin sheet lead about 7 or 8 cm. in diameter. It should be placed in a mortar just large enough to hold it, and moulded into shape by strong pressure with the pestle.

²

Calcium fluoride.		Hydrogen sulphate.		Calcium sulphate.		Hydrogen fluoride.
Ca F_2	+	H_2SO_4	=	Ca SO_4	+	2 HF

is unprotected by the wax. In about ten minutes the glass may be removed from the cup; the pungency and the acid reaction on litmus-paper of the fumes of hydrogen fluoride should be noticed, and then the cup with its contents should be dropped at once into a jug of water and afterwards well washed out, in order that the glass bottles in the room may not be damaged. The wax may be removed from the glass, by warming the latter on wire-gauze and rubbing it with blotting paper, and finally with a cloth dipped in turpentine; and the device will be found deeply and permanently etched into the glass.

The chief compound formed in the action of hydrogen fluoride on glass is silicon tetrafluoride, the preparation and properties of which will be described under SILICATES.

Before proceeding further it will be advisable to gain some more experience in analysis; taking, as before, single salts of an alkali-metal (such as sodium) united with one of the radicles already treated of, and examining each of them for the latter constituent. A short course, including all the radicles hitherto examined, is given in Appendix C.

30. SULPHUR.

[Symbol of atom,	S
Weight „	32 hydrogen-atoms.
Formula of molecule, S ₂	
Weight „	64 hydrogen-atoms.]

Preparation of sulphur from pyrites.

Sulphur is usually obtained from volcanic districts where it is found 'native' or uncombined; but large quantities of it are also procured from 'iron pyrites,' a very common mineral, which consists of iron united with sulphur (FeS₂). When this is heated (air being excluded) it gives off one-third of the sulphur it contains, as the following experiment will show.

Powder a small fragment of iron pyrites in a porcelain mortar

and place it in an ignition-tube. Heat it to redness in the lamp-flame, and notice that a sublimate of sulphur is formed in yellowish-brown drops in the cool part of the tube. It may be proved to be sulphur by cutting off the sealed end of the tube (which may be effected by touching it while still hot with a drop of water) and heating the sublimate gently in a *small* lamp-flame, while the tube is held obliquely so that a current of air may rise through it. The sulphur will be oxidised to sulphur dioxide (the gas formed by burning sulphur in oxygen, p. 122), which may be recognised by its odour and by its acid reaction on a piece of moist blue litmus-paper held at the upper end of the tube.

Allotropic forms of Sulphur.

The properties of common sulphur, such as its colour, brittleness, ready fusibility (at 115°), inflammability when moderately heated in air, will have been noticed already. The density of a piece of sulphur may be taken by the method explained on p. 52: it will be found to be almost exactly twice that of water.

Ordinary sulphur, in the shape of 'roll sulphur' or 'flowers of sulphur,' consists mainly of one of the three allotropic forms in which sulphur (like carbon) occurs. An account of these will be found in any text-book on chemistry; the following experiments will illustrate the modes of preparing them.

1. S_8 (octohedral sulphur). This is the most stable form, and the one in which sulphur nearly always crystallises from solutions of it.

Place about a gramme of 'flowers of sulphur' in a dry test-tube, and pour over them about 5 c.c. of carbon disulphide. Leave the tube, loosely corked, in a beaker of warm¹ water for a few minutes, shaking it occasionally. Care must be taken that there is no lighted lamp or fire near at hand, on account of the inflammability of the carbon disulphide. There will be a residue left, not necessarily because there is not sufficient

¹ 30 c.c. of boiling water mixed with the same volume of cold water will do. It should not be so hot as to cause the carbon disulphide to boil.

disulphide to dissolve the substance, but because the flowers of sulphur consist of two varieties of the element, of which one only is soluble in carbon disulphide. Filter the fluid quickly into another tube, through a small, perfectly dry filter. Pour the solution into a watch glass, and leave it on the table to evaporate. The carbon disulphide, from its great volatility, will quickly pass off, and small transparent crystals of sulphur will be formed and rapidly increase in size. They may be easily recognised, especially if a magnifier is used, to be rhombic octohedra, fig. 87.



Fig. 87.

2. S_{β} (prismatic sulphur). This is the form in which sulphur is obtained by crystallisation from a melted state.

Place some pieces of roll sulphur in a small evaporating dish¹, and heat it gently on a sandbath over a lamp until the sulphur is just melted; adding more sulphur by degrees until the dish is nearly full of the liquid. As soon as the whole has liquefied, remove the dish to the table and allow it to cool until a crust forms at the edges and long crystals begin to shoot across the surface towards the centre. Then, without delay, pour out the portion which is still fluid into a large dry test-tube (for use in the next experiment). The interior of the dish will be found lined with needle-shaped transparent crystals, fig. 88, which are referred to the oblique prismatic

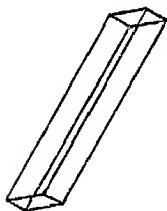


Fig. 88.

(or monoclinic) system, a system totally distinct from that to which the crystals obtained from solution in expt. 1 belong (fig. 87). In a few days the prismatic crystals lose their transparency, and are spontaneously converted into aggregations of minute octohedra.

3. S_{γ} (plastic sulphur). This is the most remarkable form

¹ The experiment is best made on a rather larger scale, a common clay crucible about 10 cm. in height being used instead of the dish.

of the three, and is obtained by the action of heat upon ordinary sulphur.

, Take the large test-tube containing the sulphur poured off from the crystals in the last experiment, add a little more sulphur and support it in a slanting position on a piece of wire gauze in the retort stand, resting it in the smallest retort ring. Lay a cork loosely in its mouth (to prevent entrance of air) and heat it, gently at first, by an argand burner, turning the tube round frequently, to equalise the heat. While it is being gently heated, fill a jug with cold water, and place in its mouth downwards a large funnel. The sulphur will first melt to a clear pale-yellow fluid, almost as mobile as water. Pour a few drops of it into some water in a dish: it will solidify into the usual yellow, brittle mass. Heat the remainder more strongly, putting a Bunsen's burner under the wire-gauze and turning the tube slowly round (the gas may be lighted above, as well as below the gauze). As the temperature rises higher the liquid will darken in colour and become thicker and thicker, until it has so far lost its fluidity that the test-tube may be inverted for a moment without spilling any of it. When the heat is further raised it becomes again fluid, but not so much so as at first. When it has reached this point, take hold of the test-tube with a paper holder (p. 68), and pour its contents in a thin stream into the cold water in the jug, round (not into) the stem of the funnel. By being thus suddenly cooled, the sulphur will be preserved in the allotropic condition into which it has been converted by heat, and on lifting the funnel out of the water, the threads of sulphur which surround it will be found to be semi-transparent, soft, almost as elastic as india-rubber, and scarcely soluble in carbon disulphide. If the residue in the test-tube be watched as it cools, it will be seen to undergo the same changes as when it was being heated, but in a reverse order, becoming thick, then losing its dark colour and becoming fluid again, and finally solidifying to a yellow, crystalline, brittle mass. It is only when the temperature has been raised nearly to its boiling-point that the above modification, called 'plastic sulphur,' is obtained. The elastic threads should be dried

with a cloth, and put aside in a bottle. In a few days they will be found to have lost both their transparency and their plasticity (being, in fact, reconverted into the ordinary form), but will still be in a great measure insoluble in carbon disulphide.

31. SULPHIDES.

	Formula of molecule.
[Typical examples,—Iron protosulphide,	FeS
Hydrogen sulphide,	H ₂ S
Lead sulphide,	PbS
Ammonium sulphide,	(H ₄ N) ₂ S]

These are compounds of sulphur with other radicles. Some of them can be obtained by simply heating the substances together: copper, for instance, combines with sulphur when heated, as has been already proved in expt. 3, p. 82. Sulphur will, in a similar way, combine with iron, but a higher temperature is required.

1. Preparation of iron protosulphide.

Mix about 3 grms. of iron filings with 2 grms. of sulphur, and heat them strongly in a small test-tube. The sulphur will melt and eventually boil, filling the lower part of the tube with its dark yellow vapour. When the bottom of the tube becomes red-hot, a bright glow will spread through the iron filings as the metal combines with the sulphur (just as it did with oxygen, p. 123) to form iron protosulphide. Allow the tube to cool, and keep the bronze-coloured residue for use in the next experiment.

2. Preparation of hydrogen sulphide.

[This gas is so extremely poisonous and offensive in smell that all experiments with it must be made in a draught cupboard, or in the open air. The best method of getting rid of any of the gas which escapes into the room is to place a little bleaching powder on a plate and add a few drops of dilute hydrogen chloride. This will liberate chlorine, as already explained, which will diffuse into the air and decompose the hydrogen sulphide. Do not, however, add too much acid to the bleaching powder, lest the

remedy should prove less endurable than the evil it is intended to cure.]

Hydrogen sulphide is obtained by the action of acids on many sulphides; the hydrogen of the acid uniting with the sulphur at the moment of its liberation. Iron protosulphide (the substance you lately obtained by the union of iron with sulphur) is, on the whole, the most convenient for the purpose.

Take the test-tube containing the iron protosulphide made in the last experiment and detach the substance from it by an iron wire (this will probably result in breaking the tube, since the substance becomes fused into the glass by the heat evolved in its formation). Powder the lump of iron sulphide and put it into a moderate-sized test-tube, to which should be fitted by a cork a short bit of glass tubing about 4 or 5 mm. in internal diameter (which answers better than a smaller jet). Support the test-tube upright, resting in the smallest ring of the retort stand in a draught cupboard, pour 4 or 5 c.c. of dilute hydrogen chloride upon the iron sulphide, and immediately fit the cork into its place. Hydrogen sulphide will be at once given off with effervescence: the action being an ordinary double decomposition, iron sulphide and hydrogen chloride giving iron chloride and hydrogen sulphide¹.

The following properties of the gas may be examined (a few drops of strong hydrogen chloride being poured into the test-tube if the evolution of gas is slow):—

***1. Its extremely fetid smell, like that of rotten eggs.**

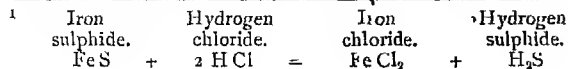
These, in fact, give off the gas; since they contain sulphur which unites with hydrogen during the process of decay.

2. Its acid reaction on litmus-paper.

Hold a bit of wetted litmus-paper close to the tube from which the gas is issuing. It will be reddened, but not very strongly.

3. Its inflammability.

Apply a light to the end of the tube. The gas will catch fire



and burn with a blue flame, uniting with the oxygen of the air to form water and sulphur dioxide¹. To prove this, invert a small dry gas bottle over the flame: moisture will be deposited on it, and the presence of sulphur dioxide in it will be proved by its characteristic odour, and the strong acid reaction shown when a piece of blue litmus-paper is put into the bottle.

Notice that some sulphur is deposited on the sides of the bottle, especially if there is an insufficient supply of air to the jet. The cause of this is similar to that of the deposit of soot in an ordinary candle flame. Oxygen has a greater affinity for hydrogen than for sulphur, and hence, when there is not enough oxygen to unite with both, some sulphur is left uncombined.

4. Its solubility in water.

One volume of cold water dissolves about three volumes of hydrogen sulphide; the method of making the solution, which is much used in the laboratory as a test, is given on p. 275.

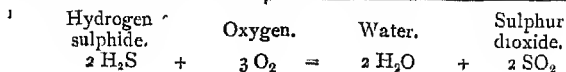
*5. Its action on compounds of lead, turning them black.

Pour a drop of solution of lead acetate upon a bit of white blotting paper and hold it in the stream of gas issuing from the tube. It will immediately turn black, owing to the formation of lead sulphide.

This is the most delicate test for the presence of hydrogen sulphide, and will serve, for instance, to detect the presence of traces of it in ordinary coal gas.

6. Its decomposition by chlorine.

Put a small gas bottle, inverted, over the tube from which the gas is issuing, so that the tube projects some way up into the bottle; and leave it in this position, supported by a retort ring, for about a minute (the gas is slightly heavier than air, but the bottle can be thus sufficiently filled). Meanwhile put a little bleaching powder (about as much as will lie on the end of a spatula) into a similar gas bottle, pour on it a few drops of



strong hydrogen chloride to liberate chlorine (as in expt. 2, p. 243) and lay a glass plate over the mouth of the bottle (which should, of course, be placed in the draught-cupboard). When the first bottle is fairly full of hydrogen sulphide, which may be tested by holding a bit of blotting paper soaked in lead acetate near its mouth, place it (still inverted) upon the mouth of the bottle containing chlorine, and withdraw the glass plate covering the latter. The gases will slowly mix, and the chlorine will decompose the hydrogen sulphide, combining with its hydrogen and liberating sulphur, which will be deposited in the bottles¹.

This illustrates the employment of chlorine as a disinfectant (already alluded to, p. 235) to destroy the hydrogen sulphide and other offensive and poisonous gases given off from putrefying organic substances.

7. Its decomposition by hydrogen nitrate.

Add to a little strong solution of hydrogen sulphide a few drops of strong hydrogen nitrate, and warm the mixture. A milky deposit of sulphur will be formed, since the acid readily gives up oxygen which unites with the hydrogen of the gas.

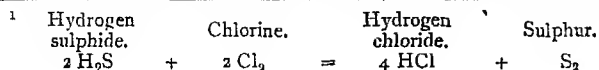
Hence we learn that in the course of an analysis hydrogen sulphide should never be added to solutions which contain much free hydrogen nitrate or chlorine.

Similarly, the solution of the gas is decomposed by the oxygen of the air; and hence it is best to keep it in a closely-corked bottle, inverted in a glass of water.

8. Its use in testing for metals.

This depends upon its property of decomposing many metal-salts when in solution, the sulphur of it uniting with the metal to form a sulphide. Many of these sulphides are insoluble in water, some even in acids, and their colours are often very characteristic.

To illustrate this, take dilute solutions of the following metal-salts (three or four drops of the ordinary laboratory solution



to 5 c.c. of water), and add to each several drops of solution of hydrogen sulphide.

(a) Copper sulphate. A *black* precipitate will be formed, of copper sulphide.

(b) Arsenic chloride ¹. A *yellow* precipitate will be formed, of arsenic trisulphide.

(c) Zinc sulphate. A *white* precipitate will be formed, of zinc sulphide.

Tests for Sulphides.

***1. They are, in general, decomposed by acids, giving off hydrogen sulphide.**

(a) Add a few drops of dilute hydrogen sulphate to a little solution of ammonium sulphide, and warm the mixture. Hydrogen sulphide will be given off, and may be recognised by its odour and its action on a strip of blotting paper moistened with a drop of solution of lead acetate. Moreover, if the solution of ammonium sulphide has been made some time and has become yellow, a white, milky precipitate of sulphur will be produced ². We learn from this that ammonium sulphide (a test very commonly employed in the laboratory) should never be added to a solution containing a free acid.

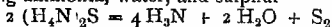
(b) Add 2 or 3 c.c. of strong hydrogen chloride to a small quantity of antimony sulphide. No decomposition will in this case take place until the liquid is boiled, when hydrogen sulphide will be given off, and may be recognised by lead acetate paper in the usual way. This is a process which is sometimes used with advantage for obtaining the gas.

***2. Their solutions, when tested with silver nitrate, give a black precipitate.**

Dilute two or three drops of solution of ammonium sulphide with 5 c.c. of water and add a drop of solution of silver nitrate.

¹ This may be made by dissolving a very small quantity of arsenic trioxide (white arsenic) in a few drops of hydrogen chloride.

² The reason is, that ammonium protosulphide slowly absorbs oxygen from the air, forming ammonia, water, and sulphur—



and the sulphur combines with another portion of the sulphide to form ammonium disulphide, from which it is separated when an acid is added.

A black precipitate of silver sulphide will be formed, which will not dissolve on addition of dilute hydrogen nitrate.

***3. They are decomposed by fusion with potassium hydrate, yielding potassium sulphide, soluble in water.**

Powder in a porcelain mortar a small bit (about the size of a pea) of iron protosulphide or of iron pyrites; add a bit of potassium hydrate¹ about the same size, and grind the whole thoroughly together. Fill the bulb of an ignition-tube with the mixture, and heat it to full redness in a Bunsen's burner for half a minute. The potassium hydrate will decompose the iron sulphide, with formation of potassium sulphide. Before it cools, dip the bulb into a few drops of water in an evaporating dish, when it will crack to pieces and the potassium sulphide will dissolve in the water. The presence of a sulphide in the solution may be proved by the blackening which takes place when a drop of the liquid is put upon a clean silver coin, or a piece of blotting paper moistened with lead acetate.

This is the best way of detecting the presence of a sulphide in minerals such as galena (lead sulphide), blende (zinc sulphide), or the golden-yellow scales which often occur in coal, and which are iron persulphide (iron pyrites); and the experiment should be tried with at least one of the above.

Additional Experiment.

Preparation of solution of Hydrogen sulphide.

Apparatus required—Flask fitted with cork, elbow-tube, and tube funnel, as used in Ex. 12, p. 188; retort-stand; wire-gauze; two elbow-tubes, fig. 32, p. 31, two ditto, fig. 33, p. 32; two wide-mouthed bottles, holding about 200 or 300 c.c., fitted with corks; cork-borers; rat-tail file; india-rubber connectors.

Iron protosulphide; strong common hydrogen chloride; distilled water.

This is a reagent which, as already indicated, is constantly required in the laboratory, in spite of its offensive and poisonous properties. In most laboratories a stock of it is kept ready, but

¹ Sodium carbonate will also answer the purpose, but the temperature required for the decomposition is higher.

the student should, if time permits, learn the way of making the solution for himself:

Bore two holes in the cork fitted to one of the wide-mouthed bottles, and fit into one hole a short elbow-tube and into the other the long branch of one of the other tubes; passing it so far through the cork that it may reach nearly to the bottom of the bottle. Adapt elbow-tubes to the other bottle in a similar way, and fill both bottles about three-fourths full of distilled water¹.

Place in the flask about 20 grms. of iron protosulphide, previously broken by a hammer into lumps about as large as peas (sliding the pieces down the neck, held slanting), and arrange it on the retort stand with a piece of wire-gauze beneath it, at such a height that the elbow-tube may be conveniently connected by india-rubber tubing with the elbow-tube passing into the water in one of the bottles. Connect the bottles by a short bit of india-rubber tubing in such a way that the gas from the flask may bubble through the water in each bottle successively, as shown in fig. 89.

[In the figure a small wash-bottle containing a little water is shown, interposed between the flask and the first of the larger bottles. This is not necessary, but is useful in order to retain any vapour of hydrogen chloride or other impurities which may come over with the gas. If used, it may be supported upon a glass or wooden disc placed on one of the rings of the retort-stand as shown in the figure.]

The whole apparatus should be placed in a draught-cupboard; or at any rate all gas which escapes from the last bottle should be led through a long tube out of the window, or into a chimney or stove-flue in which there is a good draught².

Pour into the flask just enough distilled water to cover the iron sulphide, and carefully try the tightness of every joint in the usual way: observing that the tube funnel is long enough to contain the rather high column of water which will be forced up into it.

Having ascertained that the joints are tight, pour into the flask a little strong hydrogen chloride. The evolution of hydrogen sulphide commences without the application of heat (although some

¹ It is an advantage to boil this water for about a quarter of an hour previously, in order to free it from air; allowing it to cool, of course, before placing it in the bottles. This obviates the decomposition of some of the hydrogen sulphide by the oxygen which ordinary water always holds in solution.

² Or the gas may be led to the bottom of a tall jar, filled with lumps of pumice or coke moistened with a solution of caustic soda.

little time may elapse before the action begins), and, if the stream is not too rapid, the greater part of the gas is absorbed by the water in the bottles. You will observe, however, that some gas passes through the water unabsorbed. This consists mainly of hydrogen, the evolution of which is due to the presence of uncombined iron in the sample of iron sulphide.

When a steady stream of hydrogen sulphide has passed through the bottles for five or six minutes, disconnect the first bottle, and

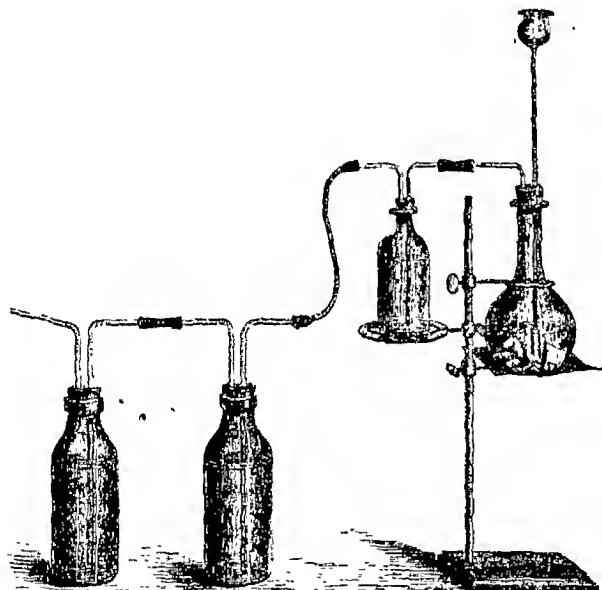


Fig. 89.

L. J. F.

connect the other directly with the flask. Ascertain whether the water is saturated with the gas, in the following way. Take out the cork and tubes, close the bottle tightly with the thumb or palm of the hand, and shake it briskly for a few seconds in order to bring the water thoroughly in contact with the gas. Hold the bottle in a slanting position with its mouth downwards, and relax the pressure of the hand, noticing whether any bubbles of air enter the bottle, or whether on the contrary the liquid is forced outwards. In the latter case the water is fully saturated with the gas; in the former

case the bottle must be again connected with the flask as at first, and more gas passed through it.

When no more gas is absorbed by the water in the first bottle, it may be withdrawn, and a little more gas passed through the water in the second bottle, which is already partially saturated by the excess of gas which has passed through the first bottle. The whole of the solution should then be poured into a larger bottle, which should be kept, well corked, in an inverted position, resting in a tumbler or test-glass half full of water.

Finally, take the apparatus to pieces at once, in the open air, and throw away the contents of the flask, washing it out thoroughly with water.

COMPOUNDS OF SULPHUR WITH OXYGEN.

32. SULPHUR DIOXIDE.

[Formula of molecule, SO_2
Weight „ 64 hydrogén-atoms.]

Apparatus required—Flask, elbow-tubes, &c., used in Ex. 12. p. 188; one large and six small gas bottles; gas jar, 20 x 5 cm.; taper on wire; glass disc; deflagrating jar and cup; basin of water.

Small strips of sheet copper; strong common hydrogen sulphate; sulphur; blue litmus-paper; solution of logwood or a little common violet ink made from magenta; a few flowers, such as roses, violets, or pansies.

Sulphur dioxide is the product invariably formed by synthesis when sulphur is burnt in oxygen or air, as seen already, p. 122. It is, however, usually prepared by a process of analysis, *viz.* by the action of mercury or copper upon hydrogen sulphate, the exact nature of which will be explained later.

The gas is very soluble in water, and should therefore be collected by displacement, which, from its great density, may be readily accomplished. It is very corrosive and poisonous, and hence it should be prepared and all experiments made with it in a draught-cupboard.

Preparation of Sulphur dioxide.

Arrange an apparatus similar to that used in preparing carbon dioxide (fig. 81, p. 188)¹. Place in the flask about ten or twelve small strips of sheet copper², add 60 c.c. of strong common hydrogen sulphate, and heat cautiously. The chemical change is analogous to that which occurs when copper acts upon hydrogen nitrate (p. 172); hydrogen is first displaced from the acid by the metal, and this 'nascent' hydrogen acts upon another molecule of the acid, taking away some of its oxygen with formation of sulphur dioxide and water³.

The action scarcely commences until the boiling point of the acid is reached (about 340°C.) and the gas is rendered cloudy at first by particles of the acid which are thrown up as spray; these, however, soon subside, and their presence will not interfere with the experiments. Collect one large and five small bottles of the gas, using a lighted taper, as in the case of hydrogen chloride, to ascertain when the bottles are full.

[Reserve the large bottle for use in Exercise 34.]

Properties of Sulphur dioxide.

*1. Its suffocating odour will have been already sufficiently noticed.

2. Its high density, more than twice that of air.

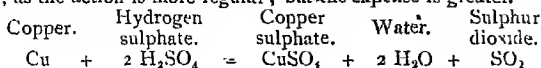
3. Its relation to combustion.

These two properties may be illustrated, as in the case of hydrogen chloride (p. 237), by placing a lighted taper in an empty gas jar, and pouring sulphur dioxide upon it.

*4. Its solubility in water, forming an acid.

¹ It is advisable, though not necessary, to interpose a small wash-bottle containing a little water, to retain any spray of acid which may come over.

² It is slightly preferable to use about 20 grms. of mercury instead of the copper, as the action is more regular; but the expense is greater.



Replace the stopper of a bottle of the gas by a glass plate, invert it, and withdraw the plate under water in the supplementary pan of the pneumatic trough (or a basin). On shaking the bottle so as to wet the sides, the gas will be readily, though not suddenly, absorbed.

In this case, as already noticed, p. 122, an acid, hydrogen sulphite, is formed¹, as may be proved by dipping a piece of blue litmus-paper into the solution.

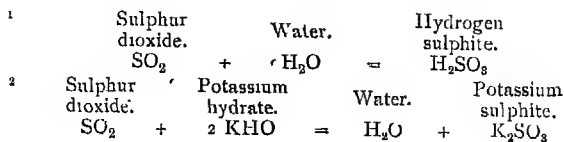
5. Its combination with metal-oxides or hydrates to form sulphites.

Pour 10 c.c. of solution of potassium hydrate into a bottle of the gas, inserting a strip of paper between the neck and the stopper, and shake up the solution with the gas. Combination will readily take place, and the odour of the gas will entirely disappear, potassium sulphite being formed².

*6. Its bleaching action on organic colours.

(a) Take 20 c.c. of a rather dilute solution of logwood or cochineal, or of the dye known as 'magenta' (made by boiling a little of the substance in water for a few minutes); pour about half of it into a bottle of sulphur dioxide, reserving the other half in the tube for comparison; put a strip of paper between the neck and the stopper, and shake the bottle for half a minute: then pour out the liquid into a test-tube. It will have nearly or quite lost its colour.

(b) Put a deflagrating jar on a plate containing a little water, and place it in some flowers, such as roses, violets, and pansies, previously wetted with water. Heat a little sulphur in a deflagrating cup, until it begins to burn in air, then place it in the jar. The sulphur dioxide produced will more or less quickly take away the colours from the flowers; the reds and the blues being soon bleached, while the greens resist a prolonged action of



the gas. It does not, however, discharge the colour so completely as chlorine, and if the flowers are dipped in very dilute hydrogen sulphate, and left for some hours, their colour will be in most cases restored.

This experiment illustrates the chief practical use of sulphur dioxide, viz. in bleaching flannel, straw for hats, &c.

Additional Experiments.

1. Action of sulphur dioxide on hydrogen sulphide.

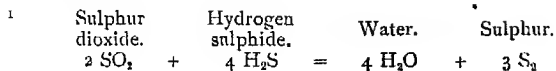
Make a little hydrogen sulphide by putting a very little powdered iron protosulphide into a small gas bottle and pouring on it a few drops of strong hydrogen chloride. Cover the mouth of the bottle with a glass plate and leave it in a draught-cupboard for a minute to fill with gas. Take a small bottle of sulphur dioxide, replace its stopper by a glass plate, invert it over the bottle containing hydrogen sulphide, and remove the plates so that the gases may mix. A cloud of sulphur will be slowly deposited in the bottles, owing to an action of the following kind:—The oxygen of the sulphur dioxide unites with the hydrogen of the hydrogen sulphide, forming water; while the sulphur-atoms in both gases combine to form molecules of sulphur¹.

This illustrates the way in which molecules of elements can be built up of atoms derived from different sources, as already mentioned under HYPOCHLORITES, p. 242, and IODIDES, p. 258. It also shows the action of sulphur dioxide as a disinfectant in destroying sewer-gases.

The deposits of sulphur found near volcanoes were probably formed by an action of the above kind between the gases issuing from the volcano.

2. Combination of sulphur dioxide with oxygen, to form sulphur trioxide.

Sulphur, as already seen, will not directly combine with more than two atoms of oxygen: but sulphur dioxide can be made to take up another atom of oxygen under the influence of heated platinum.



Make a small coil of platinum wire as directed under AMMONIA, p. 154; heat it to redness in a Bunsen's burner, and hold it while still hot just within the mouth of a bottle of sulphur dioxide. White clouds of sulphur trioxide (SO_3) will be formed by the union of the sulphur dioxide with the oxygen of the air which is entering the bottle. Observe that the combination only goes on while the platinum is hot, and that the heat of the chemical action is not enough to keep up the temperature of the platinum, as in the experiment with ammonia above alluded to. The action soon ceases, and the platinum must be again heated in the lamp in order to start it afresh.

33. SULPHITES.

	Formula of molecule.
[Typical examples,—Hydrogen sulphite,	H_2SO_3
Sodium sulphite,	Na_2SO_3]

These are salts containing the sulphite radicle (SO_3), and are usually prepared (as already seen, expts. 4 and 5, p. 280) by the action of sulphur dioxide on metal-oxides or hydrates.

Properties of Sulphites.

[A solution of sodium sulphite (freshly made) containing 1 grm. of the salt in 40 c.c. of water may be used.]

*1. When acted on by hydrogen sulphate they give off sulphur dioxide.

Add a few drops of strong hydrogen sulphate to a little of the solution of sodium sulphite placed in a test-tube, and warm the mixture. Sulphur dioxide will be given off, and may be recognised by its smell. If a slip of paper moistened with solution of lead acetate is held within the tube it will not be altered in colour.

2. When acted on by nascent hydrogen they give up oxygen, with formation of hydrogen sulphide.

Pour 5 or 6 c.c. of dilute hydrogen sulphate upon a bit of granulated zinc in a test-tube; hydrogen will, of course, be given off. Now add a drop (not more) of solution of sodium sulphite, and test the escaping gas with moist lead acetate paper, laid on the mouth of the tube, which will shortly be

blackened. The hydrogen has decomposed the hydrogen sulphite (formed by double decomposition when the sodium sulphite was added to the acid), with formation of water and hydrogen sulphide¹.

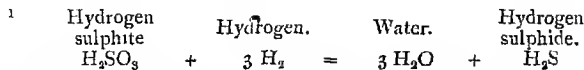
*3. Their solutions readily absorb more oxygen, with formation of sulphates.

This property renders hydrogen sulphite one of the most useful reducing agents for laboratory use: but solutions of sulphites cannot be kept long unchanged, since they absorb oxygen from the air.

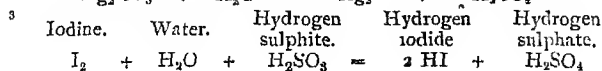
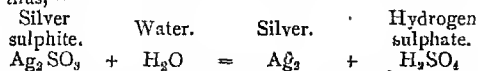
(a) To some of the solution of sodium sulphite add a drop or two of solution of silver nitrate. A white precipitate of silver sulphite will be formed, which will on being warmed turn gray owing to reduction of the silver to the metallic state: part of it being deposited as a bright mirror on the sides of the tube².

(b) Acidify a little of a very dilute solution of potassium iodide with hydrogen chloride, and add one drop of solution of chlorine (or of potassium nitrite) in order to liberate iodine, which, on addition of some solution of starch, will give a deep blue solution (p. 255). Add to this a few drops of solution of sodium sulphite; the solution will immediately become colourless, showing that the iodine has entered into combination. The change really consists in the decomposition of water; its oxygen uniting with the hydrogen sulphite, while its hydrogen unites with the iodine to form hydrogen iodide³.

Observe that this is just the reverse of the action which takes place between hydrogen iodide and *strong* hydrogen sulphate, p. 258. This illustrates the effect which the degree of dilution has in modifying chemical action.



² The action consists in the decomposition of water by the silver sulphite; thus,—



34. SULPHATES.

[Typical examples,—Hydrogen sulphate,	Formula of molecule. H_2SO_4
Sodium sulphate,	Na_2SO_4
Calcium sulphate,	CaSO_4
Copper sulphate,	CuSO_4]

These are salts containing the sulphate radicle, a group of atoms represented by the formula SO_4 . They are related to sulphur trioxide (the formation of which has been illustrated already in expt. 2, p. 282), in the sense that they can be formed by the union of metal-oxides with it, and that they can be made to yield it by proper treatment. The most important of them is hydrogen sulphate (sulphuric acid); from which, in fact, nearly all the other sulphates are prepared.

Preparation of Hydrogen sulphate.

The process by which this is manufactured on a large scale depends on the fact that sulphur dioxide, though it does not readily combine with free oxygen (except under the influence of platinum as shown already), will yet take up oxygen from nitrates and nitrogen tetroxide, reducing them to the condition of nitrogen dioxide. Thus sulphur trioxide is formed, which, when water is added, combines with it to form hydrogen sulphate. To illustrate this:—

1. Take the large bottle of sulphur dioxide reserved in Exercise 32, pour into it from a pipette 3 or 4 drops (not more) of strong hydrogen nitrate, and shake it so as to wet the sides. Orange vapours will be formed, consisting of nitrogen tetroxide; and a white crystalline substance will be deposited on the sides of the bottle, composed of the elements of sulphur dioxide and hydrogen nitrate.

In about a minute, when the action has ceased, pour into the bottle 1 c.c. (not more) of water, replace the stopper, and shake the bottle so as to bring the water into contact with the crystals. They will dissolve with effervescence, and if the bottle is left undisturbed for a minute or two all orange vapours

will disappear, the sulphur dioxide having reduced the hydrogen nitrate with formation, in presence of water, of hydrogen sulphate and nitrogen dioxide as above explained¹.

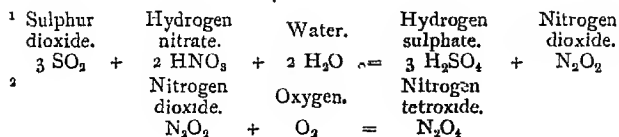
¹ But there is a further advantage in employing this reaction, for nitrogen dioxide will do what sulphur dioxide will not do, i.e. will readily take up and combine with free oxygen from air (see expt. 3, p. 174). To show this—

2. Take out the stopper from the bottle, so as to admit air. Orange vapours will again appear in it, as the nitrogen dioxide combines with oxygen to form nitrogen tetroxide².

Now it is easy to see that by mixing more sulphur dioxide with this nitrogen tetroxide, and also adding water, we should get more hydrogen sulphate formed by the reduction of the nitrogen tetroxide to dioxide as in the first reaction explained above: and then, by admitting more air, the nitrogen dioxide would again become the tetroxide. In fact, we have in these nitrogen oxides substances capable of transferring oxygen from air to sulphur dioxide. Starting, then, with a small quantity of nitrogen dioxide (obtained from hydrogen nitrate by the first reaction given above), if a continual supply of (a) air, (b) sulphur dioxide, (c) water, be kept up, an indefinitely large quantity of hydrogen sulphate can be produced.

This is the principle of the process by which nearly a million tons of sulphuric acid are made per annum in England alone; for the details of its manufacture a text-book on general chemistry must be consulted.

3. To prove that a sulphate has been really formed in the above experiments, pour into the bottle a little more water, shake it up, and pour the solution into a test-tube. Add to it a drop of solution of barium chloride, which will produce a white precipitate, insoluble on addition of a few drops of strong



hydrogen nitrate. This is, as has been mentioned already on pp. 75 and 159, a test characteristic of a sulphate.

[Another process, by which a very concentrated kind of sulphuric acid is made, called 'Nordhausen acid' and used for dissolving indigo, is mentioned on p. 398.]

Properties of Hydrogen sulphate.

[Care must be taken in dealing with the strong acid, owing to its corrosive and poisonous nature. If any is spilled on table or clothes, a little solution of ammonium carbonate should be applied, and then water.]

1. Its oily consistency and high density (1.84) will have been noticed already. The exact density of the acid you are using may be determined as directed on p. 50, if this has not been already done.

2. Its volatility at a high temperature.

Place a small drop of the acid on a piece of platinum foil and heat it over a lamp. It will volatilise entirely at 340° (nearly the point at which mercury boils), and its vapour will form dense white fumes owing to its combination with the moisture in the air.

3. Its strong acid reaction.

Put a single drop of hydrogen sulphate into 100 c.c. of water, and observe that even this extremely dilute solution reddens litmus-paper.

4. Its intense affinity for water.

This is shown by the heat evolved when the acid is diluted with water, which will have been observed already (pp. 157, 230).

(a) Put 10 c.c. of the strong acid into a small beaker placed on a plate, and mix with it quickly 5 c.c. of water. The temperature will rise above the boiling point of water, as may be proved by immersing a thermometer in the liquid.

A white turbidity will be noticed to occur when common sulphuric acid is diluted. This consists of lead sulphate (formed by the action of the acid upon the leaden troughs in which it is concentrated), which, though soluble in strong acid, is much less so in dilute acid or water, and is therefore precipitated.

[The diluted acid may be kept for use in expt. 7.]

Owing to this property it decomposes many organic substances which contain the elements of water, combining with the latter and separating carbon, as the following experiments will show.

(b) Place a drop of the acid with a glass rod upon a bit of white wood, such as a match or a shaving. The wood will turn brownish black; for the cellulose of which it is composed is a combination of carbon with hydrogen and oxygen, the two latter being present in the proportions in which they form water; and hydrogen sulphate combines with these latter, leaving the carbon.

(c) Dip the end of a glass rod into dilute hydrogen sulphate (the ordinary laboratory solution), and draw letters with it upon a piece of writing paper; then dry the paper by holding it before a fire, or at a little distance above a lamp. The acid, as it becomes concentrated, will act upon the paper (which is of the same chemical constitution as wood) in the manner above explained, and the letters will appear in black, owing to the separation of carbon.

Owing to this affinity for water, hydrogen sulphate is of great use in the laboratory for drying gases. For this purpose the gas is either allowed to bubble through a wash-bottle containing the acid (as mentioned in reference to hydrogen chloride, p. 236, note), or passed through a wide tube filled with small pieces of pumice soaked in the acid, as described in Appendix A.

[Bottles containing the strong acid must be kept tightly closed (with glass stoppers, not corks), or the acid will attract so much moisture from the air that (besides becoming useless for many purposes) it will overflow and cause damage. The bottles of this and other strong acids should be kept on a plate of glass laid on the shelf, and not placed in contact with the wood of the shelf.]

5. Its action on metals and metal-salts, forming sulphates.

The sulphate radicle (SO_4) has so strong an affinity for most of the metals that hydrogen sulphate is one of the most effective and useful agents for dissolving metals and forming metal-salts.

Several illustrations of this will have been noticed already in the course of work; for instance, its action on zinc (p. 127), on potassium nitrate (p. 158), on sodium chloride (p. 230); and many other examples of its employment will be found in Sect. III. The following experiment will illustrate its action on metal-oxides, which is applied to the preparation of numerous sulphates.

Put a little copper oxide into a test-tube, add 5 c.c. of water, and then 3 c.c. of hydrogen sulphate, and heat it to boiling over a lamp. The copper oxide will dissolve, copper sulphate and water being formed¹. If the blue solution, after filtration from any undissolved oxide², is concentrated by evaporation in the usual way (p. 62), crystals of copper sulphate (blue vitriol) will be obtained.

Additional Experiments.

6. Action of hydrogen sulphate upon sugar.

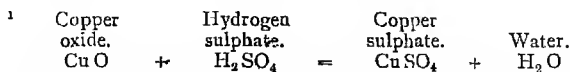
Cane sugar resembles wood and paper in composition, and like them is decomposed by the strong acid, which combines with the elements of water, leaving the carbon.

Dissolve sufficient white sugar (about 30 grms., or three ordinary lumps) in 20 c.c. of water to form a syrup, place it in a beaker standing on a plate, add to it an equal volume of strong common hydrogen sulphate, and stir the mixture. It will become hot and blacken, and will finally swell up into a porous, pasty mass of charcoal.

7. Formation of 'parchment paper.'

Hydrogen sulphate, when cold and slightly diluted, does not decompose paper in the manner illustrated in expt. 4c, but alters its texture, making it remarkably tough and semi-transparent, like vellum or parchment.

Pour the diluted acid obtained in expt. 4a, after cooling it (if necessary) by holding the beaker in a stream of water, into a porcelain dish. Take a strip of white blotting-paper about 3 cm.



² An excess of acid should not be used, otherwise a white anhydrous salt is precipitated and good crystals are not formed.

broad, and immerse about two-thirds of its length in the acid for a second or two only, simply drawing it through the liquid; then place it at once in a jug or pan of water, moving it about so as to wash off the acid quickly. Lay it on a plate and wash it with two or three changes of water, adding a few drops of solution of ammonia to the last portion of water, in order to neutralise any remaining traces of acid: then hang it up to dry. When it is dry, notice the great difference in appearance and tenacity between the undipped and the dipped parts of the paper; the latter being stiff and rather elastic, and only torn with considerable difficulty. This 'vegetable parchment' is used for many of the purposes of ordinary parchment, and especially for the operation of 'dialysis,' which means the separation of a crystallisable from a non-crystallisable substance when both are mixed in a solution.

Tests for Sulphates.

[A solution of calcium sulphate (the ordinary laboratory solution), although it is scarcely stronger than lime-water, will answer for the following tests.]

***1. Their solutions, when tested with barium chloride, give a white precipitate, insoluble in acids.**

Add to a portion of the solution of calcium sulphate a drop or two of solution of barium chloride. A white precipitate of barium sulphate will be formed (even in this weak solution) which will not dissolve on the addition of a little strong hydrogen chloride, even on boiling the mixture.

This is the most delicate and characteristic test for sulphates.

***2. Their solutions, when tested with lead acetate, give a white precipitate.**

Test another portion of the solution of calcium sulphate with a drop or two of solution of lead acetate. A white precipitate of lead sulphate will be formed, nearly insoluble in cold dilute hydrogen chloride, but slowly decomposed and dissolved by it on boiling.

***3. When ignited with charcoal, they are reduced to sulphides.**

Mix together a very little calcium sulphate (plaster of Paris) with about twice as much anhydrous sodium carbonate in a

mortar; place some of the finely-powdered mixture in a cavity made in a piece of charcoal (see p. 102), and heat it strongly in the reducing blowpipe-flame for about a minute. The calcium sulphate will thus be reduced to sulphide¹, and this is decomposed by the sodium carbonate, forming sodium sulphide. When it is cool, detach the ignited mass from the charcoal, place it in a small test-tube, pour on it a little dilute hydrogen chloride, and warm it. The presence of a sulphide will be shown by the evolution of hydrogen sulphide, recognisable by its smell and the blackening of a piece of blotting-paper moistened with solution of lead acetate, when held in the tube.

This illustrates the usual mode of detecting a sulphate in minerals such as alabaster, heavy spar, &c., which are hardly acted on by acids.

35. THIOSULPHATES

(formerly called **HYPOSULPHITES**).

Formula of
molecule.

[Typical examples,—Sodium thiosulphate, $\text{Na}_2\text{S}_2\text{O}_3$
Silver thiosulphate, $\text{Ag}_2\text{S}_2\text{O}_3$]

These are salts containing a radicle, represented by the formula S_2O_3 , which only differs from the sulphate radicle (SO_4) in containing an atom of sulphur in place of one of the atoms of oxygen (SO_3S instead of SO_3O). In fact, just as a molecule of a sulphite will readily absorb an atom of oxygen and form a sulphate (hydrogen sulphite, for instance, H_2SO_3 , becoming hydrogen sulphate, H_2SO_4 , as already proved), so it can be made to take up an atom of sulphur, and thus become a thiosulphate. Sodium sulphite readily does this, as the following experiment will show.

¹ $\text{Ca SO}_4 + \text{C}_2 = \text{Ca S} + 2 \text{CO}_2$

Preparation of Sodium thiosulphate.

Mix about 2 grms. of crystallised sodium sulphite with about half a gramme of flowers of sulphur: put the mixture into a test-tube, add 10 c.c. of water, and boil it on a sandbath for about 5 minutes. The sulphur will be slowly dissolved with formation of sodium thiosulphate, as above explained¹.

Filter the liquid from any undissolved sulphur, and prove that it contains a thiosulphate by tests 2 and 4.

This experiment illustrates the mode in which very large quantities of sodium thiosulphate are made for use in photography and paper-making.

Properties of Thiosulphates.

[A solution of sodium thiosulphate containing 1 grm. of the salt in 20 c.c. of water may be used.]

*1. They are decomposed by heat, giving off sulphur.

Heat a small quantity of crystallised sodium thiosulphate in an ignition-tube. It will fuse and give off water of crystallisation (which should be absorbed by a twisted strip of blotting paper); and finally a yellow sublimate of sulphur will form in the tube. The residue in the bulb consists of a mixture of sodium sulphide and sodium sulphate².

*2. They are decomposed by acids, giving off sulphur dioxide and depositing sulphur.

Add to a portion of the solution of sodium thiosulphate a few drops of strong hydrogen sulphate, and warm gently. Sulphur dioxide will be given off (recognisable by its smell, &c.) and a milky deposit of sulphur will be formed. In this case hydrogen thiosulphate is first formed by the usual double decomposition; and this almost immediately breaks up into hydrogen sulphite and sulphur³. The hydrogen sulphite, when heated, gives off sulphur dioxide.

¹ Sodium sulphite. Sulphur. Sodium thiosulphate.

² $\text{Na}_2\text{SO}_3 + \text{S}_2 = 2 \text{Na}_2\text{S}_2\text{O}_3$

³ $4 \text{Na}_2\text{S}_2\text{O}_3 = \text{Na}_2\text{S} + 3 \text{Na}_2\text{SO}_4 + 2 \text{S}_2$

⁴ $2 \text{H}_2\text{S}_2\text{O}_3 = 2 \text{H}_2\text{SO}_3 + \text{S}_2$

Observe the difference between this result and that given by sulphites: the latter, when treated with an acid, (expt. 1, p. 282), give off sulphur dioxide but yield *no* deposit of sulphur.

***3. Their solutions, when acidified, readily absorb oxygen.**

This is owing to the formation of hydrogen sulphite in the way explained just above. In fact, thiosulphates may be conveniently used instead of sulphites for many purposes of reduction; especially as their solutions, so long as they are kept neutral, are much more stable than those of sulphites.

(a) Make a very dilute solution of free iodine as directed in expt. 3 b, under SULPHITES, p. 283: add to it a little solution of starch to form the blue compound, and then a few drops of solution of sodium thiosulphate. The blue colour will disappear as when a sulphite was used, and for a similar reason.

This illustrates the employment of sodium thiosulphate in volumetric analysis, for determining the amount of iodine present in a solution.

(b) Put about 2 c.c. of solution of chlorine into a test-tube, add an equal volume of solution of sodium thiosulphate, and shake the mixture. Notice that the colour and smell of chlorine have now disappeared, and that the solution will not bleach indigo or liberate iodine from potassium iodide. The chlorine, in fact (like the iodine in the previous experiment), has entered into combination with the hydrogen of water: the oxygen of the latter being appropriated by the thiosulphate¹.

This illustrates the employment of sodium thiosulphate on a large scale in paper-manufacture, to destroy the last traces of chlorine (used in bleaching the rags from which paper is made), which would injure the paper if allowed to remain in it.

***4. Their solutions, when tested with excess of silver nitrate, give a white precipitate, quickly turning black.**

To another portion of the solution of sodium thiosulphate

¹ Sodium thiosulphate. Water. Chlorine. Sodium sulphate. Hydrogen chloride. Sulphur.
 $2 \text{Na}_2\text{S}_2\text{O}_3 + 2 \text{H}_2\text{O} + 2 \text{Cl}_2 = 2 \text{Na}_2\text{SO}_4 + 4 \text{HCl} + \text{S}_2$

add silver nitrate, drop by drop, shaking after each addition. The white precipitate of silver thiosulphate which is formed redissolves at first, while the sodium thiosulphate is in excess, but when more silver nitrate is added, it remains in the liquid, but rapidly changes in colour, becoming yellow, brown, and finally black. These changes are due to its instability: in presence of water it is rapidly converted into black silver sulphide¹.

5. Their solutions dissolve many compounds of silver.

This is due to their tendency to form double salts of silver which are soluble in water, as shown in the first part of the preceding experiment.

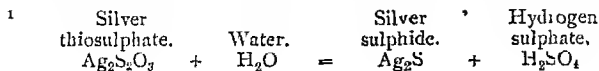
Form a little silver chloride by mixing a few drops of solution of silver nitrate with excess of ammonium chloride, wash it twice by decantation, then pour upon it some solution of sodium thiosulphate. This will form silver thiosulphate, which will unite with more of the sodium thiosulphate to form a double salt, sodium-silver thiosulphate, which dissolves readily in water.

This illustrates an important use of sodium thiosulphate in photography for 'fixing' the picture; i.e. dissolving out of the film all silver compounds unacted on by light, as will be more fully shown under SILVER.

36. PHOSPHORUS.

[Symbol of atom,	P
Weight ,,	31 hydrogen-atoms.
Formula of molecule,	P ₄
Weight ,,	124 hydrogen-atoms.]

[It is necessary to repeat that phosphorus is a rather dangerous substance to deal with. Only small pieces should be taken for



the experiments, and the precautions given on p. 81 must be strictly attended to¹.

Source of Phosphorus.

Phosphorus is obtained from calcium phosphate, a compound of calcium, phosphorus, and oxygen, which forms the chief part of the mineral matter in bones. The process by which the element is obtained cannot well be carried out on a small scale: but the first stages of it may be illustrated as follows:—

Heat a small fragment of bone to redness in a clear fire², until all the animal matter (gelatine, &c.) has been burnt away and nothing but a white, porous, earthy skeleton is left. Grind this 'bone-ash' to powder and boil it in a test-tube with about 10 c.c. of dilute hydrogen sulphate for a couple of minutes. Notice the effervescence at first, due to the decomposition of the calcium carbonate present; the main portion of the ash, however, consists of calcium phosphate, from which most of the calcium is separated by the acid as insoluble calcium sulphate, while calcium-hydrogen phosphate remains in solution³. This latter salt, under the name of 'superphosphate,' is extensively used for fertilising land. Leave the liquid to cool and deposit the calcium sulphate; then filter it, and keep the filtrate to be tested for an orthophosphate when the properties of phosphates have been examined.

It is from this calcium-hydrogen phosphate that phosphorus is obtained by igniting it with charcoal: for the details of the process a text-book on general chemistry should be consulted.

¹ As the burns produced by phosphorus are usually severe and slow to heal, it may be worth mentioning that lint soaked in water containing a little common washing soda is the best application at first. After the hydrogen phosphate is by this means neutralised, nothing is better than lint soaked in a mixture of equal volumes of glycerine and water, the whole being covered with oilskin to prevent evaporation.

² If this is not at hand, a gas-furnace, or a Bunsen's burner may be used: it should be placed in a draught-cupboard on account of the offensive smell of the gases evolved.

³ Calcium phosphate. Hydrogen sulphate. Calcium sulphate. Calcium-hydrogen phosphate.
 $\text{Ca}_2(\text{PO}_4)_2 + 2 \text{H}_2\text{SO}_4 = 2 \text{CaSO}_4 + \text{CaH}_4(\text{PO}_4)_2$

Properties of Phosphorus.

1. Its colour, softness, and insolubility in water will have been noticed already.

2. It readily dissolves in carbon disulphide.

Place about 2 c.c. of carbon disulphide in a small dry test-tube, add a small fragment of dry phosphorus about half the size of a pea, and cork the tube. Leave it to digest for a few minutes, until wanted for use in expt. 4, shaking it occasionally to promote the solution of the phosphorus.

3. It melts easily (at 44°) and catches fire when heated slightly above its melting-point.

Place a very small fragment of phosphorus (not larger than a grain of wheat), carefully dried by blotting-paper, on a watch-glass, and float it on hot water in a basin. The phosphorus will melt and shortly inflame spontaneously, giving off white fumes of phosphorus pentoxide, and leaving a small residue consisting of 'red' phosphorus, an allotropic form of the element.

4. It inflames spontaneously in air when in a finely divided condition. •

(a) Pour the clear solution obtained in expt. 2 upon a piece of blotting-paper placed on a plate (best in a draught-cupboard). The phosphorus will, as the carbon disulphide evaporates, be left in a state of fine division upon the paper; it will emit white fumes, and appear faintly luminous in the dark, and will shortly catch fire and burn away. The paper itself will be found to be only superficially charred, owing to the protective action of the phosphorus pentoxide formed.

(b) Cut off the head of a match and boil it with 4 or 5 c.c. of water in a test-tube. The phosphorus in the match will volatilise in the steam and burn within the tube with a faint greenish glow, easily seen in a dark room. If the tube containing the boiling liquid is briskly shaken, the whole of the space above the liquid is filled with the phosphorescent light.

5. It reduces many metals from their salts.

Place a small bit of phosphorus in a test-tube, pour on it

about 1 c.c. of solution of silver nitrate, and leave it undisturbed for a few hours. A bright crystalline coating of metallic silver will be formed on the phosphorus, the latter having decomposed the silver nitrate owing to its affinity for oxygen, while the metal is separated.

Properties of 'Red' or 'Amorphous' Phosphorus.

This is an allotropic form of the element, obtained by the long-continued action of heat upon ordinary phosphorus. It differs remarkably from the ordinary form, especially in the following points.

1. It is dark red, brittle, and insoluble in carbon disulphide.

Shake up a very little of the powdered substance with 2 c.c. of carbon disulphide in a test tube. No solvent effect will be observed, and if the liquid is poured out on a piece of blotting-paper no glow or ignition will take place.

2. It does not melt or catch fire at the temperature of boiling water, but inflames at a much higher temperature.

Put a little red phosphorus on a watch-glass floating on nearly boiling water as in expt. 3 (p. 295). It will not melt or catch fire, or show any alteration. If, however, it is touched with a red-hot wire, it will inflame, burning with the same bright light, and emitting the same white fumes of the pentoxide as ordinary phosphorus.

3. When strongly heated, it volatilises without melting, and is converted into ordinary phosphorus.

Place a very little red phosphorus in an ignition-tube, connect the outer end of the tube by an india-rubber connector with a glass jet (the object being to check admission of air), and heat the phosphorus very carefully over a lamp. It will sublime without previously melting; and will condense in the cooler part of the tube in amber-coloured transparent drops, which are easily recognized as being ordinary phosphorus.

Additional Experiments.

Preparation of Hydrogen phosphide and Potassium hypophosphite.

Both of these substances are formed when phosphorus is heated in a strong solution of potassium hydrate. In this action water is decomposed; part of its hydrogen unites with some phosphorus to form hydrogen phosphide, while the rest of the hydrogen together with the oxygen unite with potassium and phosphorus to form potassium hypophosphite¹.

[The following experiment must be made in a draught-cupboard or in the open air, since hydrogen phosphide is not only an extremely poisonous and offensive-smelling gas, but also spontaneously inflammable.

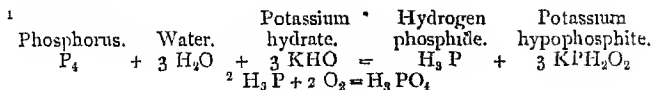
Put some strong solution of potassium hydrate (10 grms. dissolved in 20 c.c. of water) into a small evaporating dish, add a piece of phosphorus about as large as a pea, and heat the solution gently on a sandbath, taking care that it does not boil. Hydrogen phosphide will be given off, as above explained, and each bubble as it reaches the surface of the liquid will catch fire spontaneously, combining with the oxygen of the air, and forming a white smoke-wreath of hydrogen phosphate².

After allowing the action to go on for about half an hour (stopping it, however, if a brisk effervescence sets in, which would show that the potassium hypophosphite was being decomposed with evolution of hydrogen), set the dish aside (in the draught-cupboard) to cool. When it is quite cool, decant the contents into a test-tube, and immediately fill up the dish with water, to prevent the remaining phosphorus catching fire before it can be thrown away.

The solution of potassium hypophosphite may be used to illustrate the reducing action of hypophosphites as described below.

Reducing action of Hypophosphites.

Add two or three drops of solution of silver nitrate to the solution of potassium hypophosphite obtained in the last experiment and heat the mixture to boiling. The brown precipitate of silver oxide, which is at first formed, will turn black owing to its reduction to metallic silver: the hypophosphite combining with oxygen to form potassium phosphate.



37. PHOSPHORUS PENTOXIDE.

[Formula of molecule, P_2O_5

Weight „ 142 hydrogen-atoms.]

This is the only important compound of phosphorus with oxygen, and is the one which is always produced when phosphorus is burnt with a full supply of oxygen or air.

Place a small piece (about twice as large as a pea) of carefully dried phosphorus upon a plate: set fire to it with a match, and cover it with a deflagrating jar, slightly raised above the plate by short bits of glass rod or tube placed under its lower edge, so as to allow free excess of air. The stopper should be inserted in order to check the upward draught, which would carry off a portion of the product. Dense white fumes of phosphorus pentoxide will be formed, and will be deposited partly on the sides of the jar, partly on the plate. It should be used for the following experiments without delay, on account of its great tendency to deliquesce in damp air.

38. PHOSPHATES.

[Typical examples—

Formula of molecule.

Hydrogen phosphate	H_2PO_4
Sodium phosphate	Na_3PO_4
Sodium-hydrogen phosphate	Na_2HPO_4
Sodium-ammonium-hydrogen phosphate	$Na(H_4N)HPO_4$
Calcium phosphate	$Ca_3(PO_4)_2$
Calcium-hydrogen phosphate	$CaH_4(PO_4)_2$

These (which should strictly be called 'orthophosphates' to distinguish them from the less known salts pyro- and metaphosphates) are salts containing a radicle consisting of 1 atom of phosphorus and 4 atoms of oxygen (PO_4).

As will be seen from the above list, several different proportions of an electro-positive radicle (p. 85) may be associated with this electro-negative radicle. In fact, taking hydrogen orthophosphate (H_2PO_4) as a starting-point, each of the three

atoms of hydrogen in it can be replaced by an equivalent quantity of another radicle. For this reason the substance is called a 'tribasic acid' (a general text-book should be consulted for a fuller account of basicity and valency).

Preparation of Hydrogen phosphate.

This can be readily obtained by the combination of phosphorus pentoxide with water, for which it has a very strong affinity. A molecule of it will, in fact, combine with the elements of 1, 2, and even 3 molecules of water to form three distinct acids or hydrogen salts¹; only one of which is of much practical importance, *viz.* that which is formed by the union of a molecule of phosphorus pentoxide with three molecules of water. This is the ordinary 'phosphoric acid,' and may be obtained in the following way.

Remove the deslagrating jar in which the phosphorus pentoxide was just now made, and pour a few drops of water upon the white powder lying on the plate. It will hiss, as a piece of red-hot iron would do, from the heat due to the intensity of the chemical combination. Each molecule of it has now combined with at least one molecule of water to form an acid, as may be proved by dipping a piece of blue litmus-paper into the liquid. Notice also that the portions of it deposited on the sides of the jar will, after a few minutes' exposure to the air, deliquesce into drops of liquid.

The pentoxide has not yet, however, combined with the maximum proportion of water: to make it do so, heating with excess of water is necessary. Rinse the contents of the jar and the plate with a little water into a porcelain dish, and evaporate it until the liquid becomes syrupy, then add a little more water, and boil the solution again for a short time; finally filter it into a test-tube. You have now a solution of hydrogen orthophosphate from which other phosphates may be prepared by such methods as were explained under SULPHATES (p. 288).

¹ $\text{P}_2\text{O}_5 + \text{H}_2\text{O} = 2 \text{HPO}_3$ —Hydrogen metaphosphate.
 $\text{P}_2\text{O}_5 + 2 \text{H}_2\text{O} = \text{H}_4\text{P}_2\text{O}_7$ —Hydrogen pyrophosphate.
 $\text{P}_2\text{O}_5 + 3 \text{H}_2\text{O} = 2 \text{H}_3\text{PO}_4$ —Hydrogen orthophosphate.

Preparation of Sodium-hydrogen phosphate.

Pour the solution of hydrogen orthophosphate, obtained in the last expt., into a porcelain dish (reserving a little, to be added in case too much sodium carbonate may be inadvertently mixed with the rest); heat it and add solution of sodium carbonate to the hot liquid, until the addition of it no longer produces effervescence, and the liquid is slightly alkaline to test-paper. In this action two out of the three atoms of hydrogen in the acid are replaced by sodium, and a salt called 'sodium hydrogen phosphate' (the common 'phosphate of soda') is obtained¹. The solution may be evaporated to the crystallising point, and the crystals proved to be a phosphate by tests 2 and 3.

[The mode of preparing calcium-hydrogen phosphate has been already mentioned, p. 294.]

Properties of Orthophosphates.

[A solution of sodium-hydrogen phosphate, containing 3.5 grms. of the salt dissolved in 50 c.c. of water, may be used.]

***1. Their solutions, when mixed with solution of calcium sulphate, give a white precipitate, soluble in hydrogen acetate.**

Add to a little of the solution of sodium-hydrogen phosphate about half its volume of solution of calcium sulphate. A white precipitate of calcium phosphate will be formed, which will readily dissolve on addition of a little hydrogen acetate (this distinguishes it from calcium oxalate, p. 220).

***2. Their solutions, when warmed with excess of a strongly acid solution of ammonium molybdate, give a yellow precipitate.**

Pour some solution of ammonium molybdate, made strongly

¹ Hydrogen phosphate. Sodium carbonate. Sodium-hydrogen phosphate. Water Carbon dioxide.
 $\text{H}_2\text{PO}_3 + \text{Na}_2\text{CO}_3 = \text{Na}_2\text{HPO}_4 + \text{H}_2\text{O} + \text{CO}_2$
 The salt should strictly be called 'disodium-hydrogen phosphate,' in order to indicate the number of sodium-atoms in the molecule.

acid with hydrogen nitrate, into a test-tube, and add a drop or two of the solution of sodium-hydrogen phosphate. The solution will become yellow, and on warming it (it should not be boiled) a yellow precipitate will fall.

This is an extremely delicate and characteristic test for phosphates if properly used. The precautions necessary in applying it are, (a) the solution of ammonium molybdate must be used in excess, (b) it must be *strongly* acid, (c) it should not be heated to boiling, otherwise a precipitate of hydrogen molybdate is liable to form.

***3. Their solutions, when tested with magnesium sulphate, in presence of ammonium salts, give a white crystalline precipitate.**

To another portion of the solution of sodium-hydrogen phosphate add one-fourth its volume of solution of ammonium chloride, then a little ammonia, and test it with a drop of solution of magnesium sulphate. A white crystalline precipitate of magnesium-ammonium phosphate will be formed, which will readily dissolve in dilute hydrogen nitrate.

4. Their solutions, when tested with silver nitrate, give a yellow precipitate, soluble in hydrogen nitrate, and in ammonia.

To another portion add a drop of solution of silver nitrate. A canary-yellow precipitate of silver phosphate will be formed. Pour off one-half of the fluid in which the precipitate is suspended into another test-tube, and add a few drops of dilute hydrogen nitrate; to the remaining half add the same quantity of ammonia; in both cases the precipitate will be redissolved.

***5. Their solutions, when tested with iron perchloride, give a yellowish white precipitate, insoluble in acetates.**

Add to another portion of the solution of sodium-hydrogen phosphate one drop (not more) of solution of iron perchloride. A dull yellowish-white precipitate of iron phosphate will be formed. Divide the mixture into two portions.

(a) To one portion add excess of hydrogen acetate. The precipitate will remain undissolved.

(b) To the other portion add excess of iron perchloride, and

warm it. The precipitate will be redissolved. This shows the reason why only a *small* quantity of iron perchloride should be used in applying the test.

[The insolubility of iron phosphate in hydrogen acetate is important since it enables us, in the course of an analysis, to separate the phosphate radicle from certain phosphates (such as those of barium, strontium, and calcium) which are soluble in an acid but are reprecipitated without decomposition when the free acid is neutralised. To illustrate this mode of separation—

Form a little calcium phosphate as directed in expt. 1; add to this just enough hydrogen acetate to redissolve it, and then add a drop of iron perchloride to the solution. A precipitate of iron phosphate will be produced, the calcium remaining in solution as calcium chloride.]

Additional Experiments.

It has been explained above (p. 299) that a molecule of phosphorus pentoxide may combine with 1, 2, or 3 molecules of water, forming three distinct acids—hydrogen metaphosphate, hydrogen pyrophosphate, and hydrogen orthophosphate—from each of which a series of salts is derivable, having very different properties. For a full account of these a general text-book must be consulted; it will be sufficient to observe here that the salts examined above belong to the series of orthophosphates, and that from them pyrophosphates and metaphosphates can be obtained by selecting a salt from which it is possible to drive off just the requisite quantity of the elements of water by heat.

Pyrophosphates.

[Typical example,—Sodium pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7$).]

Sodium pyrophosphate is obtained by heating the ordinary sodium-hydrogen orthophosphate, with which experiments were made just now. When strongly heated, two molecules of this latter salt give off one molecule of water, leaving a residue of the pyrophosphate.

Place a few crystals of the salt in a platinum capsule, or in a cup of platinum foil made as directed, p. 8, and heat it gently at first, afterwards to redness. The salt will melt and give off its water

of crystallisation, and at a higher temperature two molecules of it will give off one molecule of water, leaving a white earthy-looking residue consisting of sodium pyrophosphate¹. This should be powdered, dissolved in about 20 c.c. of *cold* water, and examined by tests 3 and 4 in exactly the same way as directed in the case of the orthophosphate. The following results should be obtained:—

3. Tested with ammonium chloride, ammonia, and magnesium sulphate, no precipitate will be obtained (if enough solution of ammonium chloride has been added): but on warming the liquid a white precipitate of magnesium pyrophosphate will fall.

4. Tested with silver nitrate, a perfectly white granular precipitate of silver pyrophosphate will be obtained, soluble in hydrogen nitrate and ammonia.

Metaphosphates.

Typical example,—sodium metaphosphate (NaPO_3).]

To obtain this it is necessary to drive off a larger amount of the elements of water from an orthophosphate, and hence a salt must be selected which contains more hydrogen as a basic radicle, and less of a non-volatile radicle such as sodium. Such a salt is sodium-ammonium-hydrogen phosphate, or microcosmic salt, the formula of which has been given already, p. 298.

Heat a little of this salt in a platinum cup, exactly as directed in the preparation of the pyrophosphate. The substance froths up very much, and gives off ammonia and water²; finally a transparent, glassy residue of sodium metaphosphate will be left. This should be powdered, dissolved in 20 c.c. of *cold* water, and examined by tests 3 and 4 as above.

3. Tested with ammonium chloride, ammonia, and magnesium sulphate, no precipitate will be formed, if enough ammonium chloride has been added.

4. Tested with silver nitrate a white precipitate will be formed, soluble in hydrogen nitrate and ammonia.

It will be seen that these results scarcely distinguish metaphosphates from pyrophosphates, but the following test is highly characteristic of the metaphosphates; *viz.* their property of coagulating albumen (white of egg).

¹ $2 \text{Na}_2\text{HPO}_4 = \text{H}_2\text{O} + \text{Na}_4\text{P}_2\text{O}_7$

² $\text{Na}(\text{H}_4\text{N})\text{HPO}_4 = \text{H}_3\text{N} + \text{H}_2\text{O} + \text{NaPO}_3$

Add to some of the solution of sodium metaphosphate six or eight drops of hydrogen acetate, and then a few drops of a clear solution of albumen. A white precipitate of coagulated albumen will form at once.

Conversion of hydrogen metaphosphate and pyrophosphate into the orthophosphate.

This change is easily effected by boiling either of them with water; the additional amount of water being quickly taken up. To illustrate this—

Add a few drops of hydrogen nitrate to some of the solution either of sodium pyrophosphate or of sodium metaphosphate (this will form, by double decomposition, the corresponding acid), and boil for ten minutes in a beaker. Hydrogen orthophosphate will be reproduced, as may be proved by neutralising the solution with sodium carbonate and examining it by tests 3 and 4, p. 301.

39. BORATES.

	Formula of molecule.
[Typical examples,—Hydrogen borate,	H_3BO_3
Sodium diborate,	$Na_2B_4O_7$]

These are almost the only compounds of boron which are commonly met with. They are related to boron trioxide (B_2O_3), which can be obtained from them, as will be presently shown.

Preparation of Hydrogen borate.

This, although chiefly obtained from volcanic jets of steam, may also be prepared from sodium diborate (the common 'borax') by decomposing it with hydrogen sulphate: the reaction being similar to that which takes place in the preparation of hydrogen chloride and hydrogen nitrate. Since hydrogen borate is a crystallisable solid, much less soluble in cold water than in hot, it will crystallise out from a strong hot solution as the liquid cools.

Put 5 grms. of powdered sodium diborate into a test-tube and boil it with 10 c.c. of dilute hydrogen sulphate (the ordinary

laboratory solution) until a clear solution is obtained¹. Cool the liquid by holding the tube in a jug of cold water; a quantity of crystals of hydrogen borate will be gradually deposited. Pour the whole, when cold, on a small filter, rinsing out the last portions with a very little cold water, and leave the crystals to drain for a minute or two. Use some of them for the first expt. given below, and place the rest upon a porous earthenware tile, spreading them over the surface with a spatula. They will soon become fairly dry (the moisture being quickly drawn by capillary attraction into the pores of the tile) and may then be used in expts. 2 and 3.

[The tile should, after being used for any purpose of this kind, be soaked for some time in several changes of water, and dried in an oven.]

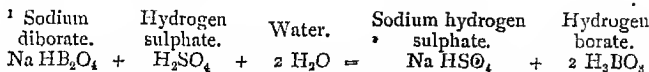
Properties of Hydrogen borate.

*1. It tinges turmeric-paper pinkish red.

Take a little hydrogen borate out of the filter on the end of a glass rod, and stir it with a few drops of water in a watch-glass until dissolved. Dip into the solution a piece of turmeric-paper, and dry it by laying it on a piece of wire-gauze held at some distance above an argand burner (or in front of a fire): as it dries, the colour of the paper will be changed to a light pinkish red.

2. When moderately heated, it is decomposed into water and boron trioxide.

Scrape up some of the nearly dry hydrogen borate from the porous tile, put it on a piece of platinum foil formed into a cup (see p. 8), and heat it to redness. It will fuse, give off water², and leave a clear glass-like residue of boron trioxide.



² Some white fumes may be also noticed: these consist of hydrogen sulphate, which was present in excess and has not been entirely separated.

***8.** It is volatile at a high temperature, and its vapour imparts a green colour to flame.

Take a little more of the hydrogen borate on a glass rod, and mix it in a small porcelain dish with about 2 c.c. of common alcohol. Set fire to the mixture, and notice the bright green colour of the flame, especially at the edges where the temperature is highest. A trace of the substance held on a ring of platinum wire in the flame of a Bunsen's burner will give a similar flame, though rather interfered with by the yellow flame due to the sodium salt from which it has not been entirely separated.

General properties of Borates.

[A solution of sodium diborate, containing 1.5 grm. of the salt in 20 c.c. of water, may be used.]

***1.** Their solutions, when mixed with barium chloride, give (if strong) a white precipitate, readily soluble in acids.

Add to a portion of the solution of sodium diborate a few drops of solution of barium chloride. A white precipitate of barium borate will be formed, which will readily dissolve on addition of a little hydrogen acetate.

***2.** Their solutions, when rendered acid, tinge turmeric-paper red.

This depends upon the formation of hydrogen borate by the action of the acid added.

Place a little solution of sodium diborate in a watch-glass, and add just enough hydrogen chloride to make the solution give an acid reaction to test-paper. Dip into the solution one-half of a slip of turmeric-paper, and dry it at a gentle heat, holding it on wire-gauze over a small lamp-flame or before a fire. The dipped portion will be coloured a rather faint pinkish red: noticeable by its contrast with the yellow colour of the undipped portion.

This may be distinguished from the brownish red produced by alkalies by placing on the paper a drop of solution of sodium carbonate, which will turn it to a blackish colour.

***3.** Their solutions, when mixed with excess of hy-

drogen sulphate and alcohol and set fire to, impart a green colour to the flame.

This, like the previous test, depends on the formation of hydrogen borate by double decomposition, as already explained. The hydrogen sulphate has also the effect of retaining in the form of non-volatile salts such substances as sodium or barium which would otherwise themselves impart a colour to the flame and thus mask the effect of the borate.

Place about 1 c.c. of the solution of sodium diborate in a porcelain dish, mix it with a few drops of strong hydrogen sulphate, then add about three times its volume of common alcohol, stir the mixture with a glass rod, and set fire to it. The edges of the flame will be tinged yellowish green, especially if the solution is stirred.

Boron trioxide and sodium diborate have the property of combining with many metal-oxides to form transparent, glass-like double salts which often possess characteristic colours. On this depends the use of borax in blowpipe work, of which several illustrations have been already given (pp. 100, 101).

COMPOUNDS OF SILICON.

40. SILICON DIOXIDE.

[Formula of molecule, Si O_2

Weight „ 60 hydrogen-atoms.]

This occurs in a pure condition as the mineral quartz or 'rock crystal'; commoner varieties of it are flint, agate, sandstone, and sand. Two methods of preparing silica (as it is often called) artificially are described below.

SILICATES.

[Typical examples,—Hydrogen silicate, $\text{H}_2\text{Si O}_3$
Sodium silicate, $\text{Na}_2\text{Si O}_3$
Aluminium silicate, $\text{Al}_2\text{Si}_2\text{O}_7$]

These are substances which contain silicon and oxygen, associated with various metal-radicles. Their composition is

often very complex, owing to the high valency of silicon, which enables it to bind several radicles into one group and form many different double salts.

A large number of minerals consist of, or contain, silicates: such as clay (aluminium silicate), slate (which is chemically the same as clay), felspar (sodium-aluminium silicate), and mica (potassium-aluminium silicate); the two last being constituents of granite. Glass also is a mixture of silicates; earthenware and porcelain are of the same chemical character. A property which all silicates possess in common is, that they can be made to yield, by methods which will be presently explained, silicon dioxide and compounds of metals.

Preparation of Sodium silicate.

To prepare this, any one of the numerous forms of silicon dioxide, such as flint or sand, may be strongly heated with sodium carbonate. In this action, the silicon dioxide simply takes the place of carbon dioxide, which latter gas escapes with effervescence¹. If a sufficient excess of sodium carbonate is taken, the resulting silicate dissolves without difficulty in water; forming, in fact, the 'soluble glass,' which is now much used in varnishes and paints.

(a) Grind about 1 gram. of flint (previously ignited, see note²) or of white sand to an extremely fine powder in a porcelain mortar, add to it about 4 grms. of anhydrous sodium carbonate³, and grind the whole *thoroughly* together. Put some of the mixture (about enough to half fill it) into a platinum capsule or a piece of platinum foil formed into a cup, and heat it to full redness over a Herapath's blowpipe (or, preferably, in a gas furnace, if at hand). It is an advantage to lay over the

¹ $\text{Na}_2\text{CO}_3 + \text{SiO}_2 = \text{Na}_2\text{SiO}_3 + \text{CO}_2$.

² If flint or quartz is to be used, it should be previously heated to full redness in a fire and quickly dropped into water. It will then form an opaque white mass, which can be more easily pulverized.

³ It is preferable to use a mixture of potassium and sodium carbonates (2.6 grms. of potassium carbonate with 2 grms. of sodium carbonate) if it is at hand; since this mixture fuses at a much lower temperature than sodium carbonate.

capsule a bit of platinum foil as a cover, in order to check loss of heat by radiation. When the mass ceases to swell up (owing to evolution of carbon dioxide as above explained) add some more of the mixture, and heat again until all action is over, and a fused glassy residue remains in the capsule. Cool this rather quickly by dipping the outside of the capsule into a little water in a dish: the sudden contraction thus produced will generally loosen the fused mass from the platinum. If not, pour a few drops of water into the capsule and boil it rather quickly over a lamp. After detaching it, grind it to powder in the mortar, adding a few drops of water; then rinse the whole into a beaker, add about 10 or 12 c.c. of water and boil it for a few minutes (meanwhile proceeding with the next expt.). The sodium silicate should almost entirely dissolve if the fusion has been properly effected, and the solution may be filtered and used for some of the following experiments.

(*b*) Powder a very little more of the flint or sand, as finely as possible. Make a ring, as described on p. 100, at the end of a piece of platinum wire; moisten it with water, dip it into some powdered anhydrous sodium carbonate, and fuse the adhering salt in the hottest part of the blowpipe flame. It will give a bead which is clear while hot, but opaque when cold. Now add to this bead some of the powdered flint and again heat it to fusion. The silica will dissolve in the bead, expelling carbon dioxide and forming sodium silicate as in the previous expt.; but the bead will probably still become cloudy or opaque as it cools. If so, add a little more silica and fuse again, using the utmost heat that the blowpipe will give. You will, when enough silica has been added, obtain a bead which is as transparent as glass when it is cold, and is, in fact, nearly the same in composition as ordinary glass. If there is any iron in the material used, the globule will be coloured more or less yellow (as bottle glass is, from the same cause); and if the bead is dipped into solution of cobalt nitrate and again strongly heated, it will be coloured blue, illustrating the mode in which various colours are imparted to glass by fusion with the oxides of certain metals.

Preparation of Silicon dioxide.

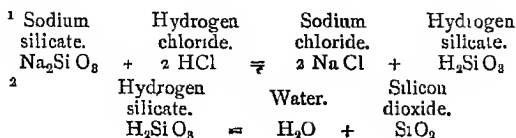
This can be obtained from sodium silicate by a process exactly the same in character as that by which boron trioxide was obtained from borax (p. 304): *viz.* by first forming hydrogen silicate by the addition of an acid, and then heating the hydrogen silicate as long as water is evolved.

Put about three-fourths of the solution of sodium silicate into a test-tube and add some hydrogen chloride, little by little, shaking the mixture after each addition. A white, gelatinous precipitate of hydrogen silicate will be formed¹, and if the solution of sodium silicate was strong, the whole will appear to solidify.

[If the solution of sodium silicate is weak, or if the experiment is repeated with a little of the strong solution diluted with five or six times its volume of water, no precipitate will be formed; the hydrogen silicate being retained in solution. But if a little of the clear liquid is added to some solution of ammonium chloride mixed with one-fourth its volume of ammonia in another tube, and heat applied, hydrogen silicate will be precipitated; since it is quite insoluble in solution of ammonium chloride.

Hence in testing for silicates, the acidified solution should always be added to a mixture of ammonium chloride and ammonia, and heated, before deciding that no silicate is present.]

Add a little water, shake up, and pour the whole on a small filter. Wash the hydrogen silicate until the filtrate is nearly or quite neutral (proceeding, meanwhile, with other experiments). Place the filter with its contents in a porcelain dish and dry it on a sandbath. Notice that the gelatinous hydrogen silicate shrinks considerably on drying, becoming a white powder. It has given off the elements of water, and is now converted into silicon dioxide².



The following properties of silicon dioxide may be tried with it, when it is thoroughly dry.

1. It is quite insoluble in acids.

Place a little of the silicon dioxide in a test-tube and boil it with 2 or 3 c.c. of strong hydrogen chloride. It will be found to be quite unacted on, and insoluble.

2. It dissolves in solution of potassium hydrate, forming potassium silicate.

Boil some of the silicon dioxide with solution of potassium hydrate. It will pretty readily dissolve. A solution of 'soluble glass' is often prepared in this way from powdered flint, instead of resorting to the fusion process.

***3. It is not acted on or dissolved by fusion with sodium-ammonium-hydrogen phosphate ('microcosmic salt').**

Make a bead of microcosmic salt in the same way as a borax bead (p. 100); heating it very gently until the water and the ammonia have been driven off (as explained on p. 303), and holding the plane of the ring horizontal, lest the melted substance (which is much more fluid than borax) should drop off.

When a perfectly clear bead of sodium metaphosphate has been thus obtained, add to it a little of the silicon dioxide and heat again. The white powder will float quite unaltered in the transparent bead.

Methods of decomposing Silicates.

The decomposition of silicates is a very frequent, and sometimes a difficult, operation in the analysis of minerals. Some silicates, especially those of the alkali-metals, are more or less readily decomposed by boiling with strong hydrogen chloride, which (as shown above) separates hydrogen silicate as a gelatinous precipitate, while a chloride of the metal is formed. But the great majority of them are best decomposed in one of the two following ways.

***1. By fusion with sodium carbonate.**

Grind a small bit of slate (aluminium silicate) or earthenware to very fine powder in a mortar, mix it intimately with about

four times its weight of anhydrous sodium carbonate, and fuse the mixture in a platinum cup precisely as directed in the preparation of sodium silicate (p. 308). During the fusion the sodium unites with the silicate radicle, forming sodium silicate, while the metal or metals (if more than one is present) are converted into carbonates or oxides.

The next step is to convert these metal-salts into soluble chlorides, and decompose the sodium silicate so as to separate silica in an insoluble form.

After detaching the fused mass from the crucible, and grinding it with a little water in a mortar, transfer it to a porcelain dish, add strong hydrogen chloride, drop by drop, until effervescence ceases, and evaporate the whole to perfect dryness on a sand-bath. It should be stirred constantly as soon as it becomes at all pasty, or portions of it will be blown out of the dish by bubbles of steam formed close to the heated surface; and the heat should be continued until the residue has lost all gelatinous appearance and become quite dry and powdery. It is then a mixture of soluble metal-chlorides (in the case of slate, aluminium and iron chlorides), and insoluble silicon dioxide; and these have next to be separated from each other.

Add to the dry mass enough strong hydrogen chloride to make it into a thin paste, and mix the whole thoroughly by gentle rubbing with a pestle; then add about 30 c.c. of water, warm the mixture, stirring it occasionally, and pour it on a filter. The filtrate will contain the aluminium, &c., as chlorides, and would in the regular course of an analysis be examined to see what metals it contained¹. The residue on the filter may, after being washed until the filtrate is no longer acid, be proved to be silicon dioxide by heating a little of it in a bead of micro-cosmic salt (see expt. 3, p. 311), in which it will float undissolved.

2. By treatment with hydrogen fluoride.

Fluorine has, as already mentioned (p. 265), a very strong

¹ If time permits, the presence of aluminium in it may be proved by trying the 2nd test given under the head of ALUMINIUM (p. 430). Iron may be very simply detected by adding to a portion of the filtrate a drop of solution of potassium ferrocyanide, which will produce a blue precipitate, characteristic of iron.

affinity for silicon, with which it combines to form a gas, silicon tetrafluoride. Thus when a silicate is heated with hydrogen fluoride, the whole of the silicon is removed and the metals remain as fluorides, which are easily dealt with.

Preparation of Silicon tetrafluoride.

[Formula of molecule, SiF_4]

Powder very finely a small bit of glass or porcelain, mix it with an equal quantity of powdered fluor spar, and put the mixture into a leaden cup (such as was used in experiments on fluorides, p. 265). Add 2 or 3 c.c. of strong hydrogen sulphate, mix the whole thoroughly, and heat it gently on a sandbath.

The hydrogen fluoride, formed by the action of the hydrogen sulphate on the calcium fluoride, decomposes the glass, and the fluorine combines with the silicon to form silicon tetrafluoride. The latter is given off with effervescence, as a colourless gas, fuming strongly in moist air. It acts, in fact, very readily upon water, forming hydrogen silicate, as may be shown thus:—

Put a drop of water on a bit of sheet glass, turn over the glass quickly, and place it, with the drop adhering to its under surface, upon the leaden cup. The drop will at once become coated with a white film of hydrogen silicate.

Besides this deposit, an acid, hydrogen fluosilicate, is formed in the reaction, as will be more fully shown in the next expt.

Additional Experiment.

Preparation of Hydrogen fluosilicate.

[Formula of molecule, H_2SiF_6]

This is an acid containing a radicle (SiF_6) analogous to the silicate radicle (SiO_3), but containing 6 atoms of fluorine in place of 3 atoms of oxygen¹.

¹ It is often called 'silicofluoride': but the name 'fluosilicate' best expresses its analogy to the silicate radicle. Compare the name 'thiocyanate,' implying a radicle analogous to a cyanate but containing sulphur in place of oxygen.

It is one of the products of the action of silicon tetrafluoride upon water; and its solution is sometimes used in the laboratory as a test for barium.

Apparatus required.—Florence flask; glass tubing, 5 or 6 mm. in internal diameter; corks; cork-boilers; fish-tail burner; argand burner; retort-stand; sandbath; gas jar, 20 × 5 cm.; tube-funnel; funnel, 10 cm. in diameter; filter, or circular piece of linen, about 20 cm. in diameter; bottle, holding 200 c.c.; test-tubes.

Fluor spar; powdered glass, or fine sand; strong common hydrogen sulphate; mercury; strontium nitrate; solution of barium chloride; distilled water.

Take a piece of glass tubing about 60 cm. long, and of rather larger internal diameter than the ordinary gas delivery-tubing. Having slightly rounded the ends in the gas-flame, bend it twice to a right angle in the same direction, making the first bend about 10 cm. from one end, and the second about 30 cm. from the other end, so as to give the tube the shape shown in fig. 90. The end of the longer branch should be bevelled off, or notched with a file on one side, to enable the bubbles of gas to escape more freely.

Select a Florence flask of stout glass (since it is liable to be corroded by the hydrogen fluoride, and will soon give way if the bottom is thin), and fit the shorter branch of the delivery-tube to it by a perforated cork.

Reduce 15 grms. of fluor spar to a coarse powder in the mortar, and mix it intimately with twice its weight of powdered glass or fine sand (that which is called 'silver sand' is the best). Pour 60 c.c. of strong common hydrogen sulphate into the flask through a tube-funnel, taking care not to wet the neck with the acid, or the cork will be destroyed. Add to it the powdered mixture and shake the whole with a circular motion until it is thoroughly incorporated. Fit the cork and delivery-tube firmly into the neck, and support the flask in the retort-stand on the sandbath, heaping up the sand round its sides, so as to distribute the heat. Place under the outer extremity of the delivery-tube a cylindrical gas jar containing a stratum of mercury about 12 mm. deep, into which the end of the delivery-tube must dip. This stratum of mercury is quite essential, since it acts as a valve and prevents the entry of water into the tube, which would then soon be obstructed by the bulky precipitate of hydrogen silicate, formed the moment that the gas comes in

contact with water. The apparatus will then appear as represented in fig. 90.

After seeing that the end of the delivery-tube is well below the surface of the mercury, and that the flask is firmly held by the retort-ring, so that the delivery-tube cannot shift its position, fill up the jar with distilled water, pouring it gently down the sides of the vessel so that none may enter the delivery-tube through a disturbance of the surface of the mercury. Heat the flask very slowly with an argand burner or spirit lamp. The reaction between the fluor spar and the acid requires only a moderate temperature, and

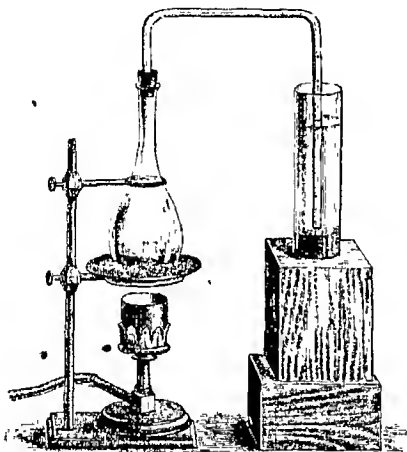
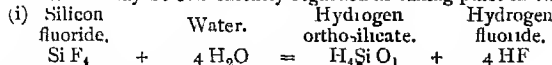


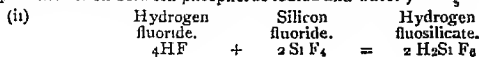
Fig. 90.

if too much heat be applied, the mixture froths up inconveniently, and may pass over into the water. When the gas begins to come over, each bubble as it emerges from the mercury becomes coated with a film of silica, which is left behind when the bubble reaches the surface of the water, as a shrunken, collapsed bag¹.

¹ The action may be conveniently regarded as taking place in two stages.



(Compare the action between phosphorus iodide and water)



Increase the heat slightly if the stream of silicon fluoride becomes slow, and continue it until no more gas comes over¹: then loosen the cork and take the delivery-tube quickly out of the solution. Filter the liquid from the gelatinous silica through a paper, or more conveniently, a fine linen filter; care being taken that none of the mercury falls on the filter. [The silica thus obtained is very pure, and hence may be worth the trouble of washing, an operation which takes some time, and must be done very thoroughly. After a final rinse with warm water, the filter containing the silica may be left to dry, either spontaneously or on a sandbath.]

It is best to keep the solution of the acid, not in glass, but in a gutta-percha bottle, since the former is always acted upon to a certain extent. Before using it as a test for barium, examine it by the two following tests, to make sure that it contains no hydrogen sulphate, which may have been carried over mechanically, if the action has proceeded too rapidly.

Properties of Hydrogen fluosilicate.

1. It produces no precipitate in solutions of strontium salts.

(a) Dissolve a few small crystals of strontium nitrate in 10 c.c. of water, and add to the clear solution about 5 c.c. of the acid which you have prepared. No precipitate will be formed, since strontium fluosilicate is soluble in water.

[If a precipitate or turbidity is produced immediately, or within a few minutes, hydrogen sulphate is present as an impurity, and the acid cannot be used for the following expt.]

2. When mixed with a solution of a barium salt, it forms a white crystalline precipitate.

Add a few drops of the acid to a little solution of barium chloride in a test-tube. A crystalline precipitate of barium fluosilicate will be formed, which will not be dissolved on the addition of some dilute hydrogen nitrate (resembling barium sulphate, p. 289, in this respect).

¹ Do not, however, apply a strong heat, or hydrogen sulphate may distil over, and render the solution useless for analytical purposes. If a strong solution of hydrogen silicofluoride be wanted, it is a good plan to set up another similar apparatus, with a delivery-tube leading into the same jar of water. The time necessary to obtain the required solution is thus diminished by one-half.

[If no precipitate forms, the solution of the acid is not sufficiently strong, and more silicon fluoride must be passed into it in the manner above described, before it can be used as a test for barium.]

[The student is recommended, before passing on to the study of the different metals, to refer to the account of the course of analysis given at the commencement of Part II, and to practise himself in the analysis of single salts containing some one of the foregoing non-metallic radicles associated with an alkali-metal. The portions of the scheme of analysis which he will require for this purpose are Section II (omitting such experiments as relate to the detection of a metal), and Section IV.]

SECTION III.

PREPARATION AND EXAMINATION OF THE PROPERTIES
OF THE PRINCIPAL METALLIC RADICLES
AND THEIR COMPOUNDS.

[Before commencing the experiments on each metal, an account of the metal itself, its ores, the mode of obtaining it from the ores, and the general characters of its compounds, should be read up in some good text-book on Chemistry, and briefly entered in the note-book.]

An account of the principle on which the metals are classified into groups is given in Part II, Section I : and such of the experiments there given as relate to the metals should be now tried.]

Group I.

Metals which are separated from solutions by hydrogen chloride.

SILVER, MERCURY, LEAD¹.

1. SILVER.

[Symbol of atom, Ag (argentum).]

Weight „ 108 hydrogen-atoms.]

	Formula of molecule.
[Compounds of silver,—Silver nitrate,	AgNO_3
„ chloride,	AgCl
„ oxide,	Ag_2O

[Liquids containing silver, such as the mother liquor from the crystals of silver nitrate and the residues from the following experiments, should on no account be thrown away, but reserved in a bottle labelled 'Silver Residues²']

¹ Mercury is only thus separated when in the monovalent condition. Lead is only partially separated, since lead chloride is not quite insoluble in water.

² For the method of recovering the silver from these residues, see Appendix B. II.

It must be borne in mind that solutions of silver salts, if allowed to touch the skin or clothes, stain them black. The quickest way of removing these stains is to moisten them first with a solution of potassium iodide, and then with strong solution of potassium cyanide. Great care must, however, be taken in using the latter, as it is very poisonous: all traces of it should be washed away as soon as it has removed the stains.]

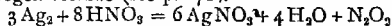
Preparation of Silver nitrate from an alloy such as silver coin.

The English silver coinage consists of silver alloyed with about one-thirteenth its weight of copper. This alloy dissolves readily in hydrogen nitrate, but the silver alone is precipitated as chloride when hydrogen chloride is added to the solution.

Place a small silver coin weighing about 1 grm. in a large test-tube, pour on it 6 or 8 c.c. of concentrated hydrogen nitrate, and warm the tube very gently on a sandbath. A strong action will commence, and nitrogen oxides will be evolved, the fumes of which should not be allowed to escape into the room¹. In a short time a clear bluish green solution will be formed, containing silver nitrate and copper nitrate. Dilute the solution with four or five times its volume of water, and add about 10 c.c. of common strong hydrogen chloride. The silver will be completely precipitated as chloride, while the copper chloride, being soluble in water, remains in the liquid. Close the mouth of the tube and shake it for a few seconds: the suspended silver chloride will then separate in curdy masses, and after adding a few more drops of hydrogen chloride to make sure that the precipitation is complete, the liquid may be poured off through a filter².

The precipitate should next be thoroughly washed on the filter with several changes of water, until the liquid which runs

¹ The action is similar to that of hydrogen nitrate on copper in the preparation of nitrogen dioxide (see p. 172).



² It may be proved to contain copper by putting a small strip of clean bright iron, or the blade of a knife, into it: a red coating of metallic copper will be deposited, as shown in expt. 1, p. 87.

through the filter ceases to redden blue litmus-paper. While the last portions of water are draining off, take a strip of sheet zinc about 1 cm. broad and 12 or 14 cm. long, cover its surface with a thin film of mercury¹ by immersing it for $\frac{1}{2}$ minute in an acid solution of mercury perchloride (2 c.c. of the ordinary laboratory solution with 20 c.c. of water and 5 c.c. of dilute hydrogen sulphate), and then wash it with clean water. Transfer the silver chloride to a large test-tube, rinsing it through a hole made in the filter: then fill the tube half full of water, add about 5 c.c. of dilute hydrogen sulphate, and put in the strip of zinc, taking care that it comes closely into contact with the mass of silver chloride at the bottom of the tube. A galvanic action will be set up, and the hydrogen liberated in contact with the silver chloride will combine with the chlorine; and thus the silver will be separated in the metallic state as a fine black powder, which, as the molecules aggregate together into larger masses, will become of a light brown, or gray. In about half an hour the reduction will be complete, and the zinc may then be taken out, and the liquid (which contains hydrogen chloride, as may be proved by testing a small portion of it with silver nitrate) poured off from the spongy mass of reduced silver. Wash the latter thoroughly by decantation (breaking up the lumps by stirring with a glass rod), boiling it with several successive changes of water, until the washings give no precipitate with silver nitrate.

[To prove that the earthy-looking powder is really metallic silver, a small portion of it may be taken out with a spatula, dried on blotting paper, placed in a mortar and pressed under a polished glass pestle. The particles will then cohere, forming a plate with a bright metallic lustre.]

After pouring off as much of the water as possible, add four or five drops of strong hydrogen nitrate, and warm the mixture; the finely divided metal will readily dissolve, forming silver

¹ This is advisable (though not absolutely necessary) since it prevents 'local action' (see under ZINC) and avoids the separation of the particles of carbon, lead, &c., which always occur in ordinary zinc, and are rather difficult to separate from the reduced silver.

nitrate. Another drop or two of the acid may be put in, if there is still a residue undissolved on warming the liquid; but any great excess of acid should be avoided. Pour the solution into a porcelain dish and evaporate it to dryness: the residue may be used for making the solution of silver nitrate required for the photographic experiment (p. 327).

Formation of double salts of Silver.

[The ordinary laboratory solution of silver nitrate, containing 1 gm. of the salt in 50 c.c., may be used.]

Silver shows a great tendency to form with the alkali-metals double salts which are, as a rule, soluble in water. One example of these, silver-sodium thiosulphate, has been given already under THIOSULPHATES.

1. Silver-ammonium oxide.

Put two drops (not more) of solution of ammonium hydrate into a test-tube, dilute with about 4 or 5 c.c. of water, and add solution of silver nitrate drop by drop. A brown precipitate of silver oxide (or perhaps hydrate) will be at first formed, but this will, on shaking, redissolve, forming a clear solution containing the double oxide of silver and ammonium ($\text{Ag}(\text{H}_4\text{N})\text{O}$). Continue adding silver nitrate gradually, shaking the mixture thoroughly after each addition, until a *slight* permanent brown precipitate is formed (showing that the ammonium hydrate is no longer in excess), and keep the solution for a future expt. (p. 323).

2. Silver-potassium cyanide.

Put about 5 c.c. of solution of silver nitrate into a test-tube, and add a few drops of solution of potassium cyanide (1 gm. in 30 c.c.). A white precipitate of silver cyanide will be formed, but when sufficient excess of potassium cyanide has been added, this will redissolve, forming a solution of silver-potassium cyanide (AgKCy_2), which is the compound usually employed in electroplating. The solution should be kept for use in a future experiment in illustration of this (p. 326).

Reduction of Silver from its compounds.

Silver is one of the easiest metals to reduce from its salts. It can be separated from an electro-negative radicle both by chemical and physical means. Its reduction from silver chloride by nascent hydrogen has lately been illustrated (p. 320); its reduction from silver nitrate by mercury was effected in an expt. given on p. 88, the principle in these and other cases being to turn out the silver by means of some substance which has a stronger affinity for the electro-negative radicle. Tartrates also, p. 217, sulphites, p. 283, and hypophosphites, p. 297, have been shown to reduce silver from its carbonate or oxide. The following experiments illustrate processes of great practical importance.

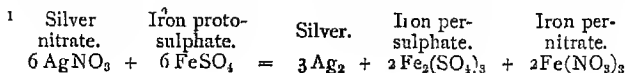
The reduction of its salts by fusion with sodium carbonate will be found described on p. 327.

1. By iron protosulphate.

Put five or six drops of solution of silver nitrate into a test-tube, dilute with 5 or 6 c.c. of water, and add a few drops of solution of iron protosulphate. No immediate change will be observed, but in the course of a minute or two a gray deposit of particles of metallic silver will form gradually, the lustre of which can be seen on shaking up the contents of the tube.

The nature of the action is this:—The iron in iron protosalts has a great tendency to combine with more of a non-metallic radicle than it holds already in combination: in doing which it changes its valency or combining power, becoming trivalent instead of divalent. Hence some of it leaves the sulphate radicle (enough still remaining to form the persulphate) and takes the nitrate radicle from its combination with silver, the latter being separated in the metallic state¹.

The gradual way in which the reduction takes place renders iron protosalts of great value as ‘*developpers*’ in photography; the silver particles, when thus leisurely separated, attaching themselves by preference to those portions of the sensitive



film of silver iodide which have been acted on by light, and thus building up an intense picture. For details a treatise on photography must be consulted.

2. By organic substances.

(a) Draw letters on a piece of paper with a glass rod dipped in a solution of silver nitrate, and heat the paper in front of a fire, or at some distance above the flame of an alcohol burner, until it is nearly hot enough to become scorched. The letters will appear in an indelible black; the hydrogen and carbon of the paper having decomposed the salt, combining with its oxygen, while metallic silver is separated, and adheres closely to the fibre of the paper.

This illustrates the use of 'marking ink,' which is simply a solution of silver nitrate thickened with gum. It also explains why silver salts stain the skin black.

(b) Tartrates (as seen already, p. 217) and some other organic compounds (e.g. grape sugar) readily reduce silver from its combinations; the action being in general similar to that of the paper in the experiment just made. When the deposition of the metal is made to take place gradually, it forms a surface equal in smoothness and polish to that of the glass vessel to which it adheres, and reflects light brilliantly.

Take the solution of silver-ammonium oxide obtained in expt. 1, p. 321, and filter it from the slight deposit of silver oxide. Add to the filtrate about two drops of solution of sodium-hydrogen tartrate, mix thoroughly, and warm it by placing the tube in a jug or beaker of hot water. The liquid will turn black, and a brilliant film of metallic silver will be deposited on the sides of the tube.

This illustrates the mode in which mirrors for telescopes (in some cases a metre or more in diameter) are covered with a firm deposit of silver, which will even bear careful polishing.

A fairly good convex mirror may be made from a watch-glass as follows. Clean the inside of it thoroughly with a few drops of solution of potassium hydrate applied with a tuft of tow or cotton, then rinse it several times with distilled water and imbed it to the edge in sand on a sandbath. Make a rather strong solution of

silver-ammonium oxide as above directed (p. 321), using 1 c.c. of solution of ammonium hydrate diluted with 5 c.c. of water : and, after adding five or six drops of solution of sodium-hydrogen tartrate, fill the watch-glass to the brim and heat the sand very gently. In about half an hour the reduction will be complete ; the liquid may then be poured off, and the deposit on the glass washed by a very gentle stream of distilled water and left to dry spontaneously. It will not be advisable to attempt to polish it : the curved film looked at through the glass will form the convex mirror.

If a concave mirror is desired, it may be made as follows. Attach a cork to the inside of a watch-glass by sealing-wax, to serve as a handle. Clean the convex side of the glass by potash as above directed, and (after rinsing it) support it, convex side downwards, in a small porcelain dish by means of three bits of wire or splinters of wood stuck into the cork like spokes of a wheel, and resting on the edge of the dish. There should be a clear interval of 5 or 6 mm. between the glass and the bottom of the dish. Ascertain by measurement with water what volume of liquid will be required to fill up the space between the glass and the dish, and make sufficient silver-ammonium oxide solution for the purpose : then proceed as already directed. The cork may be afterwards detached from the glass by putting in a little alcohol, which will soon dissolve the sealing-wax¹.

3. By the action of light.

This is especially rapid in the case of silver chloride, the alteration in colour of which, when exposed to light, may have been noticed already. The change may now be examined more fully, and the effect of the presence of excess of a soluble silver salt may be tried.

¹ A very good silvering process is that known as Martin's, an outline of which is given below.

Make the following solutions—

- | | | |
|--------------------|---------|-----------------------------------|
| A. Silver nitrate, | 2 grms. | } dissolved in 100 c.c. of water. |
| Ammonium nitrate, | 3 grms. | |
| B. White sugar, | 5 grms. | } dissolved in 50 c.c. of water. |
| Hydrogen tartrate, | 1 gm. | |

Boil this solution for ten minutes, then add 10 c.c. of pure alcohol and dilute with water to 100 c.c.

- C. Potassium hydrate (pure) 5 grms. dissolved in 50 c.c. of water.

For use, mix equal vols. of B and C (say, 10 c.c. of each) and add to the mixture the same vol. (say, 20 c.c.) of A. No heat should be used : the reduction takes place quite readily in the cold.

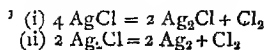
Prepare a little silver chloride by adding excess of solution of ammonium chloride to about 5 c.c. of solution of silver nitrate: wash it on a filter, avoiding exposure to light as much as possible. Take the still moist filter out of the funnel, open it out on blotting-paper, and spread the silver chloride in an even layer over it with a glass rod; then divide it into two pieces, each containing some of the precipitate, and lay them upon separate watch-glasses or plates. Pour upon one of the pieces a drop or two of ammonium chloride (to decompose any remaining traces of silver nitrate), and upon the other a similar quantity of silver nitrate; and expose them both to a good light (sunlight if possible). In about half an hour observe the difference in the results.

(a) The silver chloride which was freed from all silver nitrate will have turned bluish gray, owing to separation of some, at any rate, of the chlorine from the silver; but the reduction will be only slight and superficial.

(b) The silver chloride to which the silver nitrate had been added will be found to have turned to a brownish black, and the effect will have penetrated deeper.

The reason of the difference is this:—The effect of light is in both cases to separate chlorine from the silver chloride in two stages, forming (i) silver subchloride and chlorine, (ii) metallic silver and chlorine¹. The dark film of silver protects the portions below from the action of the light, and hence the reducing action almost ceases in (a), where we are dealing with pure silver chloride alone. But in (b), where we have some silver nitrate interspersed among the particles of the silver chloride, the chlorine liberated as above explained from each molecule of silver chloride decomposes this nitrate and forms more silver chloride, which is at once reduced by light: and so the action continues until a considerable deposit of silver is obtained.

This illustrates the action which goes on in the production



of an ordinary photographic print, which will be more fully illustrated in a future experiment.

4. By the action of electricity.

All processes of electroplating depend upon this method of reduction of silver salts; silver-potassium cyanide being found the most suitable, since the metal is deposited from it in a firm coherent film.

Pour the solution of silver-potassium cyanide already made (expt. 2, p. 321) into a small porcelain dish: put into it a clean bright strip of copper, and lay on the copper a small bit of zinc, pressing the two closely into contact (or, better, connect them as shown in fig. 96, p. 412). The copper will very shortly become coated with a white film of silver: the action being similar to that in which copper was deposited on platinum (p. 79).

Tests for compounds of Silver.

***1. Their solutions, when tested with hydrogen chloride, give a white precipitate, soluble in ammonia, but not in aqua regia.**

Put two or three drops (not more, in order that the delicacy of the test may be observed) of the solution of silver nitrate into a test-tube, dilute with 5 or 6 c.c. of water, and add a drop or two of dilute hydrogen chloride. A white, curdy precipitate of silver chloride will be produced.

(a) Pour off half the liquid containing the precipitate in suspension into another tube, add to this portion a little strong hydrogen chloride and a drop or two of hydrogen nitrate (so as to form aqua regia) and boil the mixture. The precipitate will not dissolve or be altered in any way (being thus distinguished from the precipitate of mercury protochloride, p. 340).

(b) To the remaining portion add solution of ammonium hydrate, which will readily dissolve it. If excess of dilute hydrogen nitrate is added to the clear solution, silver chloride will be again precipitated.

***2. Their solutions, when tested with potassium chromate, give a crimson precipitate.**

Add to a similar dilute solution of silver nitrate a drop or two of solution of potassium chromate. A dark crimson precipitate of silver chromate will be formed, readily soluble in dilute hydrogen nitrate.

*3. Reduced on charcoal before the blowpipe, they yield a brilliant metallic malleable globule, but no incrustation.

Powder a small crystal (no larger than a grain of wheat) of silver nitrate, mix it intimately in the mortar with about twice as much sodium carbonate; then place some of the mixture in a cavity cut in a piece of charcoal (see p. 102), and heat it cautiously in the blowpipe flame, remembering that nitrates deflagrate when heated in contact with charcoal (p. 163). When the deflagration is over, bright particles of silver will be seen, which may by increasing the heat be fused together into one globule. This will remain untarnished in the oxidising flame, and no incrustation will be observed on the cooler parts of the charcoal, since silver has but little tendency to unite with oxygen. The malleability of the globule should be tried by placing it in a clean porcelain mortar and pressing strongly on it with the pestle. It will spread out into a flat plate, and no tendency to split at the edge will be observable under a magnifier.

Additional Experiment.

Preparation of a photographic print.

The principle of this process has been illustrated already in expt. 3, p. 325.

[Solutions required,—

Ammonium chloride, 1 grm. in 50 c.c. of water.

¹Silver nitrate, 4 grms. in 50 c.c. of water

Sodium thiosulphate, 10 grms. in 50 c.c. of water.]

Pour the solution of ammonium chloride into a flat plate or dish. Take a piece of fine drawing-paper about 10 or 12 cm. square, make a small pencil-mark in one corner, then taking it up by the two opposite corners lower it gently upon the solution in the plate,

¹ The silver nitrate obtained from the silver coin, p. 321, may be used in making this solution.

keeping the marked side downwards, so that the centre touches the liquid first, the two corners being lowered afterwards, in order that no air-bubbles may be retained between the solution and the paper. Allow the paper to float upon the solution for five or six minutes, then take it up by one corner, and pin it to a shelf or the back of a chair with the wet side outwards, to drain and dry, attaching a small bit of blotting-paper to the lowest corner, to absorb the solution which drains down.

The next stage of the preparation of the paper, since it involves the formation of a compound sensitive to light, must be performed by candle-light, and therefore in a cellar, or a room with closed shutters, or in the evening. Pour the solution of silver nitrate into a perfectly clean plate, carry it into a room lighted only by a candle or by a small gas-flame, and float upon it the piece of salted paper (with the marked side downwards), taking particular care to avoid air-bubbles. The silver nitrate in the solution will act upon the ammonium chloride in the paper, and ammonium nitrate and silver chloride will be formed at the surface of the paper. After the lapse of five minutes, raise the paper by one corner and pin it up, as before, to dry in a dark cupboard or drawer. Obtain two pieces of flat window-glass, rather larger than the piece of prepared paper; lay one of them flat on the table in a room lighted by a candle (or gas) only, or at any rate in the darkest corner of a room in which the blinds are drawn down. Place upon the glass a piece of black velvet or thick brown paper; lay upon this the dry piece of prepared paper, having the marked side upwards; place upon the paper a piece of black lace or a fern leaf, or a piece of blackened card with letters cut out in it¹; and on the top of all lay the other plate of glass. Bind the whole together by two letter clips or india-rubber bands, one on each side, and bring the extempore printing-frame into full daylight. You will observe the portions of the prepared paper which are not protected by the lace or the engraving, to pass through shades of red and purple, finally becoming black and bronzed, if looked at obliquely by reflected light. When this is the case, remove the apparatus again to the dark room, and take out the prepared paper. The lace, or other opaque object, will be found to have protected the paper from the action of the light, and an image of it will be formed, white on a black ground. Of course,

¹ A small engraving, the paper of which has been rendered semi-transparent by warming the back of it and rubbing in white wax or paraffin, will answer.

if the paper was now brought out to the daylight, it would blacken all over, and the image would be obliterated. If it be thought worth preserving, it must be soaked in several changes of common water to remove all excess of silver nitrate (see note below¹), and then placed in the solution of sodium thiosulphate. This solution will dissolve away all the unaltered silver chloride (see p. 293), leaving the reduced silver untouched: a process termed 'fixing' the picture. After the print has remained about ten minutes in the solution it should be removed, and washed in several changes of water; after which it may be brought out to the light without damage. Unless the 'toning' process mentioned in the note has been employed, the black portions will have become reddish brown, and will be reduced in intensity; but the experiment will serve the purpose of illustrating the action of light on silver chloride, and the principles of the art of photography.

2. MERCURY.

[Symbol of atom, Hg (hydrargyrum).

Weight „ 200 hydrogen-atoms.]

[It must be borne in mind that mercury and most of its compounds are very poisonous, whether taken internally or absorbed by the skin. Moreover, the metal should not be spilled about on the table or floor, or thrown down the sink, since it combines with lead and soon destroys the pipes².]

Preparation of Mercury from its ores.

Mercury is chiefly obtained from its sulphide, the mineral cinnabar, which is chemically the same as vermilion. This

¹ If the print is a good clear one, it may be worth while, before applying the sodium thiosulphate, to render it more intense and permanent by the following 'toning' process. Dissolve 1 grm. of sodium diborate in 50 c.c. of water, add six or eight drops of solution of gold chloride (1 grm. in 50 c.c.) and pour the mixture over the washed print, laid on a plate; moving the paper about so that the solution may act uniformly all over it. The silver of which the picture is formed will decompose the gold chloride, forming silver chloride, and metallic gold will be deposited in its place. When the dark portions have turned bluish black, the solution should be poured off and the print after a slight washing may be placed in the solution of sodium thiosulphate as above directed.

² It is a good plan, when making experiments involving the use of metallic mercury, to place all the apparatus on a shallow tray, so as to retain any of the metal which is accidentally spilt. A common tea-tray will answer: or one may be made extemporaneously by turning up the edges of a piece of brown paper, and cementing the corners with sealing-wax.

yields the metal when heated with quicklime, the calcium and oxygen of which combine with the sulphur¹.

Powder a small bit of cinnabar or vermilion (the ordinary red paint), and mix it intimately with twice as much quicklime²; then put some of the mixture into an ignition-tube, cover it with a little more quicklime and heat it strongly. Bright globules of a liquid metal will condense in the tube, running together into one drop when scraped off the glass with a splinter of wood, such as a match. These must be mercury, since it is the only metal which is liquid at ordinary temperatures.

Properties of Mercury.

1. Its liquidity and cohesion.

Pour a few drops of mercury on a clean plate; if the metal is pure the drops will preserve their roundness as they roll about, since their cohesion to each other is much greater than their adhesion to the surface on which they rest².

2. Its high density, 13.6 times that of water.

This may be ascertained in the manner described on p. 51; 5 c.c. of mercury being carefully measured and then weighed. Owing to the strong cohesion of mercury compared with its adhesion to the glass, the curve of its surface in the tube will be convex, thus \frown , instead of concave, \smile , as in the case of water; and hence, in order to obtain an approximately correct measure, the 5 c.c. mark should coincide with the line where the liquid touches the glass (and should not form a tangent to the curve, as usual).

3. Its volatility (boiling point, 360°).

Place a small drop of mercury in a dry test-tube (using a pipette to transfer it), and heat it over a lamp, holding the tube

¹ $4\text{HgS} + 4\text{CaO} = 3\text{CaS} + \text{CaSO}_4 + 4\text{Hg}$

² If the metal contains lead or other impurity, its liquidity is impaired, and the drops will become elongated when the plate is inclined, and will move about sluggishly, leaving portions behind them. In order to purify it, pour it into a plate or shallow dish in sufficient quantity to form a thin stratum at the bottom, and pour over it enough dilute hydrogen nitrate (1 vol. of the strong acid to 20 vols. of water) to cover it. Leave it in contact with the metal for three or four hours, stirring it occasionally with

nearly horizontal. The metal will boil below a red heat, and, if pure, will wholly volatilise, its vapour condensing in the cooler parts of the tube and forming a bright metallic ring, which, when looked at through a magnifier, will be seen to consist of minute liquid globules like dew. These, if touched with a glass rod, may be made to run together into one large drop.

4. Its combination with metals, forming amalgams.

The combinations formed by one metal with another are in general called 'alloys,' but the alloys of mercury have received the special name of 'amalgams' (an old alchemical name). The amalgam of mercury and zinc has been already alluded to (p. 320), and will be more fully described under ZINC. Mercury and tin form an amalgam which is of great practical use in the manufacture of mirrors.

Clean a piece of tin-foil about 5 cm. square by rubbing over it a drop of strong hydrogen chloride with a tuft of tow held in the crucible tongs. After washing and drying it with a cloth, place it on a tray of paper (made by turning up the edges of a sheet of writing-paper) laid on a smooth flat table or block of wood. Pour on it several drops of mercury from a pipette: the mercury will at once adhere to, and amalgamate with, the tin: it should be rubbed with a tuft of tow until an even layer is formed all over the tin. Take a bit of sheet glass about as large as the tin, and, holding it horizontally, bring it to the edge of the layer of mercury, and slowly slide it over the tin so that its edge, immersed in the mercury, may sweep before it any dirt or impurities, leaving a clear bright surface of mercury in contact with the glass. Press it down on the tin with a weight of

a glass rod to expose a fresh surface of the metal to the acid; then pour off the acid, wash the mercury with a stream of water poured from a jug, and finally, after pouring off as much water as possible, absorb the remainder with a clean cloth or blotting-paper. Fit a filter in a funnel, and make two or three fine holes with a pin at the point; support the funnel over a beaker or bottle, and pour into it the dry mercury.³ The metal which runs through will be found very nearly pure; it may be further purified by distillation, but, except for special purposes, the gain in purity will scarcely compensate for the trouble and risk.

1 kilog. or more, so as to squeeze out all superfluous mercury (which should *not* be put back into the bottle¹), and leave it under pressure for a day or two. The mercury will by that time have thoroughly combined with the tin, and formed a solid, brightly-reflective amalgam on the surface of the glass.

Thus illustrates the way in which ordinary looking-glasses and mirrors are 'silvered.'

Preparation of compounds of Mercury.

Mercury forms two distinct series of compounds, in one of which a given weight of it is combined with twice as much of the electro-negative radicle as is present in the other. It is found for instance, that one atom of mercury (Hg) will saturate and form a definite crystallisable compound with either

(i) one atom² of the nitrate radicle (NO_3), to form mercury protonitrate (HgNO_3), or

(ii) with two atoms of the same radicle to form a molecule of mercury pernitrate ($\text{Hg}(\text{NO}_3)_2$).

Either one of these can be formed, to the exclusion of the other, by varying the conditions under which hydrogen nitrate acts on mercury.

The existence of these two series of compounds illustrates very well the variation which may exist in the 'valency' of a chemical atom, by which term is meant its power of holding other atoms in combination. Thus in regard to the nitrate radicle, the chlorine radicle, and others, the mercury-atom is said to be 'monovalent' in the protosalts and 'divalent' in the persalts. When salts of the one series are converted into the corresponding salts of the other series (protosalts into persalts and *vice versa*), the conversion is accompanied by a change of valency of the mercury-atom.

¹ It may be reserved for amalgamating zinc battery plates, or making sulphur dioxide.

² The word 'atom' is used here, of course, in its strict chemical sense, to express the smallest quantity which can take part in a chemical action.

A. Mercury Protosalts.

[Typical examples,—Mercury protonitrate, $\text{Hg}_2(\text{NO}_3)_2$ ¹
 „ protochloride, Hg_2Cl_2
 „ protoxide, Hg_2O]

Preparation of Mercury protonitrate.

Mercury protonitrate is prepared by taking hydrogen nitrate slightly diluted and allowing it to act on excess of the metal, the temperature being kept low².

Place a globule of mercury about as large as a pea in an evaporating dish, and pour upon it a mixture of 5 c.c. of strong hydrogen nitrate with 3 c.c. of water. Allow the action to go on for ten minutes or so (while other experiments are proceeded with), stirring the liquid frequently, but applying no heat; then pour the solution, together with the remaining mercury, into a test-tube, dilute it with water to 50 c.c., and reserve it (marked 'mercury protonitrate') for experiments, p. 341.

[In keeping solutions of mercury protosalts, some metallic mercury must always be present in the bottle or tube; otherwise the substance will soon pass into a persalt.]

Preparation of Mercury protochloride.

This is the common substance known as 'calomel,' and is usually prepared on a large scale by heating the required proportion of mercury with mercury perchloride. As a comparison of the formulæ of the molecules will show, each molecule of the perchloride (HgCl_2) requires the addition of one atom of mercury in order to form the protochloride (Hg_2Cl_2)³.

¹ The above formulæ for the molecules are used instead of the simpler ones, HgNO_3 and HgCl because the protosalts show a tendency to separate into metallic mercury and a persalt; indicating that there may be more than one atom of mercury in the molecule. This is not inconsistent, of course, with what is said above with reference to the valency of the single mercury-atom.

² $2 \text{ Hg} + 4 \text{ HNO}_3 = \text{Hg}_2(\text{NO}_3)_2 + \text{N}_2\text{O}_4 + 2 \text{ H}_2\text{O}$

³ $\text{HgCl}_2 + \text{Hg} = \text{Hg}_2\text{Cl}_2$

Place a small glass mortar in one scale of the balance, counterpoise it, and weigh into it 2 grms. of mercury and 2.7 grms. of mercury perchloride. Grind the whole thoroughly together until most of the mercury has been broken up into small particles and mixed with the perchloride. Put all the contents of the mortar into a small test-tube, and apply heat. A sublimate will form, yellow while hot, but turning white on cooling, which is mercury protochloride. Shake out some of this into another tube and heat it. Observe that it volatilises without any sign of previous fusion: passing at once from the state of solid to the state of gas. Boil a little more of it with water: it will be found insoluble. Both these properties distinguish it from mercury perchloride, which is soluble in water, and when heated liquefies before volatilising.

Preparation of Mercury protoxide (or suboxide).

Pour some solution of potassium hydrate upon some of the mercury protochloride obtained in the last expt. A black substance will be formed, which is mercury protoxide¹.

B. Mercury Persalts.

[Typical examples,—Mercury	Formula of molecule.
pernitrate,	$\text{Hg}(\text{NO}_3)_2$
,, perchloride,	HgCl_2
,, periodide,	HgI_2
,, persulphide,	HgS
,, peroxide,	HgO]

Preparation of Mercury perritate.

The conditions necessary for preparing mercury perritate are, strong acid taken in excess, and a high temperature.

Put a small globule of mercury into an evaporating dish, pour on it 4 or 5 c.c. of strong hydrogen nitrate, and heat the whole on a sandbath, in a draught-cupboard if possible². Allow the

¹ $\text{Hg}_2\text{Cl}_2 + 2 \text{KHO} = \text{Hg}_2\text{O} + 2 \text{KCl} + \text{H}_2\text{O}$

² $\text{Hg} + 4 \text{HNO}_3 = \text{Hg}(\text{NO}_3)_2 + \text{N}_2\text{O}_4 + 2 \text{H}_2\text{O}$

action to go on until all the metal is dissolved, then add a little more strong acid and continue heating it until a drop taken out on a glass rod gives no precipitate when mixed in a watch-glass with a drop of dilute hydrogen chloride¹. After driving off any great excess of acid by evaporation², pour about three-fourths of the solution into a test-tube, dilute it with water to 30 c.c. and reserve it (marked 'mercury pernitrate') for experiments, p. 342. Evaporate the remainder of the solution to dryness, and reserve the residue for making mercury peroxide (p. 337).

[The preparation of mercury perchloride has been illustrated already, p. 240.]

Formation of Mercury periodide.

This substance has been prepared already (p. 84), but not in a manner in which the remarkable change of colour which it undergoes could be noticed.

(a) Dilute two drops of a solution of mercury perchloride with 5 or 6 c.c. of water, and add one drop of solution of potassium iodide. The precipitate of mercury iodide which forms is, in this dilute solution, bright yellow at first, but changes in the course of a minute or more into pink and finally scarlet.

The reason of the change of colour appears to be this;—Mercury periodide exists in two different allotropic conditions, which differ in crystalline form: the one occurring in oblique rhombic prisms which are yellow, the other in square octohedra which are scarlet. Of these the most stable is the latter, and hence the yellow precipitate, which consists of the prismatic modification, changes to scarlet, the conversion being quicker in strong solutions.

¹ Some mercury protonitrate is at first formed; and this, as will be proved later, gives a white precipitate with hydrogen chloride, while the pernitrate does not. Hence when the solution gives no precipitate with hydrogen chloride, we may be sure that it contains mercury pernitrate only.

² If the evaporation has been unintentionally carried to dryness, a little dilute hydrogen nitrate must be used to dissolve the residue: otherwise a basic salt insoluble in water will be formed.

If a few more drops of solution of potassium iodide are added to the precipitate it will readily dissolve, a double salt, mercury-potassium iodide, being formed¹.

(d) Put a little of the scarlet mercury iodide obtained in Exercise 9, p. 92, into a small dry test-tube, and heat it slowly over a lamp. It will melt and volatilise, condensing in yellow prismatic crystals in the cool part of the tube. The yellow sublimate, however, is not permanent; on rubbing it with a glass rod scarlet lines will appear and the whole will soon pass again into the more stable modification.

[If you possess a moderately good microscope, you will find it interesting to watch the progress of the change by subliming a little of the scarlet mercury iodide from a crucible to one of the ordinary microscope slides², placing it on the stage of the instrument, examining the crystals with a one-inch power, and lightly touching one of them with a needle. The change will begin in the crystal which was touched, and gradually spread through the whole, while its progress may readily be watched; the yellow rhombic prisms, though unchanged in general shape, becoming aggregations of red octohedra with a square base, belonging to a different crystallographic system.]

Preparation of Mercury persulphide.

This substance, which is identical with vermilion, affords another example of the change of colour due to difference of allotropic form which is often observable in the compounds of mercury.

¹ The use of this as a test for ammonium salts will be described under AMMONIUM.

By dissolving a large quantity of mercury iodide in a saturated solution of potassium iodide, a liquid may be obtained which is of so high a density that glass will float in it.

² To obtain good crystals for this purpose it is necessary that they should be deposited slowly. Place a little of the mercury iodide in a small porcelain crucible, imbed it in sand on a small sandbath, and heat it over an argand burner. While it is getting hot, take a clean slip of glass (an ordinary microscopic 'slide') and heat it carefully over a lamp flame. When the mercury iodide in the crucible begins to volatilise, place the hot slip of glass on the top of the crucible, and leave it for half a minute or so. Withdraw it as soon as a slight deposit of crystals has formed, since if they are too crowded the effect is not so good.

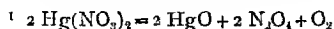
Weigh out 0.5 grms. of sulphur and 3 grms. of mercury, place them in a small test-tube and apply heat. As the temperature approaches the boiling-point of mercury, a strong action will commence, the sulphur and mercury combining to form a black mass of mercury sulphide. Continue heating this for half a minute, observing its volatility, on account of which it can be driven about from one part of the tube to another: then, after allowing it to cool, detach some of it from the tube and grind it to powder in a mortar. Lastly, shake the powder out on a sheet of writing-paper, and rub it strongly with the pestle. Observe that it changes during the grinding and rubbing from black to a dull red, leaving a streak of that colour upon the paper. The same change, which is due to the black, amorphous sulphide becoming crystalline, may be effected by a very slow process of sublimation, as in the Chinese method of making vermilion.

If, however, a little vermilion or cinnabar is heated in an ignition-tube it forms a black sublimate of the amorphous sulphide.

Preparation of Mercury peroxide.

This can be prepared by two different processes: either (*a*) by decomposing mercury pernitrate by heat, or (*b*) by the addition of potassium hydate to a solution of a mercury persalt. The colour of the oxide differs remarkably according to the mode in which it is prepared, owing to one variety being crystalline, the other amorphous.

(*a*) Scrape together the dry residue of mercury pernitrate obtained by evaporation of the solution already made (p. 335); put it into a small dry test-tube, and heat it moderately strongly. A decomposition will occur¹ exactly like that of lead nitrate under similar circumstances (p. 167); orange vapours of nitrogen tetroxide will be evolved, and also oxygen; and a residue of mercury peroxide will be left, which is quite



black while hot, but becomes red as it cools. Do not heat the tube to redness, since (as has been proved already, p. 77) mercury oxide is itself decomposed into its elements when strongly heated.

(b) Put a little of the solution of mercury pernitrate into a test-tube, and add excess of solution of potassium hydrate. A bright yellow precipitate will form, consisting of mercury peroxide, identical in composition with the red oxide obtained in the previous experiment, but amorphous; while the red oxide is easily seen to be distinctly crystalline.

General properties of Mercury salts.

*1. They are volatile at a temperature below redness.

(a) Place a small crystal of mercury perchloride ('corrosive sublimate') in an ignition-tube, and heat it gently over the lamp. The salt will fusc, and at a rather higher temperature volatilise entirely, forming a white crystalline ring in the cool part of the tube.

Observe that mercury perchloride melts before volatilising, while mercury protochloride has been proved already (p. 334) not to do so.

*2. Heated with sodium carbonate in an ignition-tube, they yield a sublimate of liquid metallic globules.

Mix a little mercury perchloride with at least twice as much anhydrous sodium carbonate in a mortar, introduce it into an ignition-tube in quantity just sufficient to half fill the bulb, and cover it with a layer of the dry sodium carbonate. Wipe the tube clean with a twisted strip of blotting-paper, and heat it very gently over the lamp. At first, if the substances are not perfectly dry, some moisture will be given off, which must be absorbed by strips of blotting-paper, before a stronger heat is applied; otherwise it will be difficult to obtain a well-defined sublimate. When no more water condenses in the tube, increase the heat, until the bulb is nearly red-hot. A metallic

sublimate will form in the tube, which, when examined with a magnifying-glass, will be seen to consist of small, round lustrous globules of mercury ¹.

§8. They are reduced by copper.

Place a drop of solution of mercury perchloride on a strip of copper freshly cleaned with emery paper. Allow it to remain for half a minute, and then wash it off. A dull gray stain will be left on the copper, which when rubbed with a cloth will become bright and silvery. The mercury salt has been decomposed, copper chloride being formed, while the mercury is deposited on the more electro-negative metal, the copper, with which it forms an amalgam.

If the copper is heated, but not to redness, the bright deposit will disappear.

Conversion of Mercury persalts into protosalts, and vice versa. Reduction and Oxidation.

It has already been shown that by varying certain conditions, such as the temperature and the proportions of metallic and non-metallic radicle, we can cause mercury to show either a higher or a lower valency, and form either a persalt or a protosalt exclusively. It will be instructive to see how we can change the valency of the mercury-radicle in an already-formed salt, thus converting a salt of one series into a salt of the other series. Such a change is called an 'oxidation' or a 'reduction' in the most general sense, without necessarily implying that oxygen has anything to do with the action. To illustrate this we may take the two mercury chlorides (which, of course, contain no oxygen whatever) and see how they can be formed from each other.

¹ Mercury iodide is the only commonly occurring mercury compound which under the above conditions volatilises unreduced, in spite of the superposed layer of sodium carbonate. It may, of course, be easily identified by its colour and its behaviour when heated alone, p. 336.

A. Conversion of a persalt into a protosalt.
(‘Reduction.’)

For this purpose we require to take away from each molecule of mercury perchloride (HgCl_2) one-half of the chlorine it contains. Tin protochloride is a convenient ‘reducing’ agent for effecting this, since it has a strong affinity for chlorine.

Put 3 or 4 c.c. of solution of mercury perchloride (the ordinary laboratory solution) into a test-tube, and add one drop (not more¹) of solution of tin protochloride.

A white precipitate will form, consisting of mercury protochloride, which (as has been proved already, p. 334) differs from the perchloride in being insoluble in water. The tin protochloride has taken away half the chlorine from the mercury salt, becoming² itself tin perchloride³. [Keep the mixture for the next expt.]

B. Conversion of a protosalt into a persalt.
(‘Oxidation.’)

To effect this in the case of mercury protochloride, we have to add to each molecule (Hg_2Cl_2) just as much chlorine as it already contains. This can be best done by using chlorine in the ‘nascent’ state when (as already mentioned, p. 239) its combining powers are most active: and aqua regia, p. 239, is the most convenient source of it.

Add to the mercury protochloride obtained in the last expt. about 2 c.c. of strong hydrogen chloride and 1 c.c. of strong hydrogen nitrate; and apply heat. The white precipitate will soon disappear, the mercury protochloride having combined with chlorine to form the perchloride³, which dissolves in the water.

¹ If more is added, the reduction will proceed farther, and metallic mercury will be thrown down, which is not the present object.

² $2 \text{ HgCl}_2 + \text{SnCl}_2 = \text{Hg}_2\text{Cl}_2 + \text{SnCl}_4$

³ $\text{Hg}_2\text{Cl}_2 + \text{Cl}_2 = 2 \text{ HgCl}_2$

General definition of Oxidation and Reduction.

Chemical compounds are formed by the union of radicles, one of which is more strongly electro-negative than the other or others, (i.e. appears at the positive electrode when the compound is decomposed by an electric current); and Reduction means the process of withdrawing from a compound some or all of the electro-negative radicle which is present in it. Oxidation is the converse change, *viz.* the addition to a substance of more of an electro-negative radicle than is already present in it.

Distinctive properties of the protosalts and persalts of Mercury.

[For the following experiments the solutions of mercury protonitrate and mercury permnitrate, which have been already prepared (pp. 333, 335), may be used.

It will be convenient to apply each test successively to the protosalt and the persalt, and to record the results in parallel columns in the note-book.]

A. Mercury protosalts.

*1. With hydrogen chloride they give a white precipitate, blackened by ammonia.

Pour a little of the solution of mercury protonitrate into a test-tube, and add a few drops of dilute hydrogen chloride. A white precipitate of mercury protochloride will be formed.

Add to this excess of ammonium hydrate. It will turn black, owing to the formation of mercury protoxide (p. 334).

This reaction distinguishes it from the other two insoluble metal-chlorides, *viz.* those of silver and lead.

*2. With hydrogen sulphide they give a black precipitate at once.

Test another portion with solution of hydrogen sulphide. A black precipitate of mercury protosulphide will be formed.

3. With potassium hydrate they give a black precipitate.

Add to a third portion some solution of potassium hydrate. A black precipitate of mercury protoxide will be formed, insoluble in excess.

B. Mercury persalts.

[The corresponding tests should be applied to the solution of mercury pernitrate in precisely the same way as directed for the protosalts.]

1. With hydrogen chloride they give no precipitate.

2. With hydrogen sulphide they give a precipitate which is at first white, but soon changes to yellow and finally black.

If the hydrogen sulphide is added drop by drop, and the liquid shaken, a precipitate will be produced which is at first white, but on further addition of hydrogen sulphide becomes yellow, brown, and finally black. The cause of this characteristic reaction is, that a combination of mercury persulphide and nitrate is first thrown down, which is converted entirely into mercury persulphide by excess of the precipitant.

(a) Pour off a little of the mixture into another tube; render it alkaline with ammonia, add some ammonium sulphide, and warm the mixture; the precipitate will remain undissolved.

This distinguishes mercury sulphide from the sulphides, insoluble in acids, of certain other metals, e.g. tin sulphide, which form soluble double salts with ammonium sulphide.

(b) Add to some more of the mercury sulphide a little strong hydrogen nitrate, and apply heat. The substance will remain undissolved.

This distinguishes mercury sulphide from all the other precipitated sulphides of this and the following group of metals: the latter are decomposed by strong hot hydrogen nitrate, forming nitrates which dissolve. Mercury sulphide is, however, decomposed by aqua regia, as may be proved by adding a few drops of hydrogen chloride to the mixture containing hydrogen nitrate. The black precipitate will readily dissolve: mercury perchloride being formed.

3. With potassium hydrate they give a yellow precipitate.

This precipitate, as already seen, p. 338, consists of mercury peroxide.

3. LEAD.

[Symbol of atom, Pb (plumbum).]

Weight " 207 hydrogen-atoms.]

The most important ore of lead, Galena (lead sulphide), is a rather common mineral, having a bright metallic lustre like lead itself, but easily distinguishable from the metal by its brittleness. If any of it is at hand, the following experiment may be tried, which illustrates the treatment applied to most metallic ores before their actual reduction; *viz.* heating in a current of air to convert them into oxides (if not so already) and render them porous and more easily acted on. This is called 'roasting' the ore.

Put a little finely-powdered galena into the bend of a tube of difficultly-fusible glass about 14 or 15 cm. long, bent to an obtuse angle about 4 or 5 cm. from one end as shown in fig. 91. Hold the tube in the position shown in the figure (the long branch being inclined upwards so as to act like a chimney, and cause a current of air to rise through the tube), and heat the



Fig. 91.

bend where the powder lies to redness in a Bunsen's burner; taking care that there is room for the free passage of air over the powder. The oxygen of the heated air will decompose the lead sulphide, combining with both its elements and forming lead oxide, which remains in the tube, and sulphur dioxide, which goes off as gas and may be recognised by its smell and its reddening action on a piece of wetted blue litmus-paper held close to the upper end of the tube.

[The density of lead, if not already taken, may be ascertained by the method given on p. 52; a bullet or a short strip of thick sheet lead being used for the purpose. Pure lead has a density of 11.45, rather higher than that of most metals, though not so high as that of mercury.]

Preparation of compounds of Lead.

	Formula of molecule.
[Typical examples,—Lead protoxide,	PbO
„ red oxide,	Pb_3O_4
„ dioxide,	PbO_2
„ acetate,	$\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$
„ chromate,	PbCrO_4]

Many of these are manufactured on a large scale for purposes of painting. Some, e.g. lead chromate, owe their value to the brilliancy of their colour; others, e. . lead protoxide, to their property of combining with oils, forming hard compounds unalterable by weather.

1. Lead protoxide ('litharge').

Cut off from a strip of sheet lead a small piece about the size of a grain of wheat, noticing the softness, pliancy, and want of elasticity of the metal. Lay it in a cavity cut in a piece of charcoal (fig. 68, p. 102), and direct the hottest part of the flame of a blowpipe upon it. It will readily melt, and when red-hot it should be removed to the oxidising flame, and the blast of air increased in strength. A film of oxide will form on the globule of metal, and will be swept off by the air-current, forming a yellow incrustation on the surrounding charcoal.

This illustrates the mode in which 'litharge' is manufactured in large quantities, and also the principle of the process of 'cupellation,' by which silver is separated from lead when alloyed with it: for when the alloy is treated in the above way, the lead is readily oxidised and separated, while the silver remains unaltered on the basin or 'cupel.'

2. Lead red oxide ('red lead').

Mix 2 grms. of lead protoxide with half a gramme of potassium chlorate, grinding the whole thoroughly together. Heat the mixture moderately, over a Bunsen's burner, in an iron spoon or capsule until all effervescence due to escape of oxygen has ceased, and then allow it to cool. The lead protoxide will under these circumstances combine with more oxygen, and a bright red residue will be obtained, containing 'red lead.'

3. Lead dioxide.

The 'red lead' obtained in the last experiment does not appear to be a very definite chemical compound. In the first place the proportions of lead and oxygen in it do not appear to be constant (see Laws of Chemical Combination in Appendix D), and in the next place it can be very easily separated into the protoxide and the dioxide in the following way.

Pour some dilute hydrogen nitrate on a little red lead in a test-tube, and warm the mixture. A chocolate-coloured powder will remain undissolved, which is lead dioxide. In fact, the red lead (Pb_3O_4) behaves as if it were a mixture of lead protoxide (2 PbO), which is acted on by the acid with formation of soluble lead nitrate, and lead dioxide (PbO_2) which is unacted on by dilute hydrogen nitrate.

4. Lead acetate ('sugar of lead').

Place 2 grms. of lead protoxide in a test-tube, add 5 c.c. of hydrogen acetate, and heat the mixture to boiling. The oxide will be readily acted upon with formation of lead acetate¹, which will dissolve. Dilute the solution with an equal volume of water, filter it from any slight residue, and keep it for use in subsequent experiments.

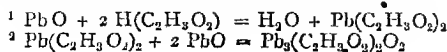
5. Lead basic acetate.

Lead acetate shows a tendency to combine with one or more molecules of the protoxide forming soluble basic acetates, which are employed in medicine and also (as will be shortly explained) in the manufacture of 'white lead' for paint.

Pour about half of the solution of lead acetate just made into a small beaker, add 2 grms. of lead protoxide, and boil the mixture for three or four minutes. A large portion of the oxide will dissolve with formation of lead basic acetate². Filter the liquid into a test-tube, observe the strong alkaline reaction of the solution, and use it in the next experiment.

6. Lead carbonate ('white lead').

This is a very valuable white paint, and is usually made by



the action of carbon dioxide on lead basic acetate. One process for making it may be illustrated as follows. Take the test-tube containing the solution of lead basic acetate made in the last experiment, and blow air through the liquid by means of a long-branched elbow-tube. The solution will shortly become turbid, the carbon dioxide of the breath combining with lead oxide from the basic acetate to form lead carbonate, which is precipitated¹. Neutral lead acetate remains in solution; and in the actual manufacture of the paint this is employed to dissolve more lead oxide, and the resulting basic acetate is decomposed by carbon dioxide as before. Thus only a small quantity of lead acetate is required to make an indefinitely large quantity of white lead. (Compare the action of the nitrogen oxides in the manufacture of sulphuric acid.)

7. Lead chromate ('chrome yellow').

Dilute a few drops of the solution of lead acetate with 5 or 6 c.c. of water, and add some solution of potassium chromate. A bright yellow precipitate will be formed, consisting of lead chromate: a most effective yellow paint, though, like other lead compounds, liable to alteration if exposed to coal-gas or smoke.

[If the precipitate is allowed to subside (which it will quickly do on being warmed), the liquid decanted off, 10 or 12 c.c. of lime-water added, and the mixture heated to boiling, the yellow colour will change to a bright red, owing to the formation of a basic lead chromate, which is used as a paint under the name of 'chrome-red.']

Properties of salts of Lead.

[The solution of lead acetate already made, diluted with 20 c.c. of water (or the ordinary laboratory solution of the salt), may be used.]

*1. Their solutions (if strong), tested with hydrogen chloride, give a white precipitate, unaltered by ammonia.

Add a few drops of dilute hydrogen chloride to some of the solution of lead acetate. A white crystalline precipitate of lead chloride will be formed, insoluble in excess of the strong acid².

¹ $\text{Pb}_2(\text{C}_2\text{H}_3\text{O}_2)_2 + 2\text{CO}_2 = \text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 + 2\text{PbCO}_3$

² A large excess of dilute hydrogen chloride will dissolve it, the effect being due, however, not to the action of the acid, but to the action of the water, as in (a).

Divide the fluid containing the precipitate in suspension into three portions, and test them as follows :—

(a) Add to the first portion three or four times its volume of water. The precipitate will gradually redissolve. Owing to this solubility in water, it is not formed at all in weak solutions of lead salts.

(b) Heat the second portion to boiling. It will in this case also redissolve, but will be reprecipitated as the solution cools, in snow-like flakes, which, when examined by a magnifier, will be seen to consist of groups of slender prisms.

(c) To the last portion add ammonia. The precipitate will not dissolve or alter in colour; being distinguished by this property from silver and mercury chlorides.

***2. With hydrogen sulphide they give a black precipitate.**

Test another portion of the solution of lead acetate with solution of hydrogen sulphide. A black precipitate of lead sulphide will be produced, insoluble in cold dilute hydrogen chloride, but decomposed on being boiled with excess of the strong acid. It will be remembered that this property of lead, of forming a black compound with sulphur, furnished a very delicate test of the presence of a sulphide (p. 272).

[To show the delicacy of this test, mix one drop of the solution of lead acetate with 200 c.c. of water, and add a few drops of solution of hydrogen sulphide. The liquid will acquire a distinct brown tinge, best seen by placing a sheet of white paper under the beaker or test-tube, and looking down through it.

This reaction is useful for detecting the presence of lead in drinking water. In applying it, the water should be previously acidified with hydrogen acetate, to prevent any compounds of iron (which may be present) from interfering with the test.]

It is owing to this action of sulphides that all paints consisting of, or containing, compounds of lead are so liable to turn brown or black when exposed to air containing smoke or coal gas.

*3. With hydrogen sulphate they give a white precipitate.

Test another portion of lead acetate with dilute hydrogen sulphate. A white precipitate of lead sulphate will be formed, insoluble in excess of the acid, but readily decomposed and dissolved if warmed with solution of ammonium acetate¹.

[Since lead sulphate is slightly soluble in hydrogen chloride, the best method of applying this test is as follows :—

* Make a very dilute solution of lead acetate by mixing 5 c.c. of water with two drops of the ordinary solution, and add two or three drops of ammonia. This will produce a white precipitate of lead hydrate. Now add to the liquid excess of dilute hydrogen sulphate; this will decompose the hydrate, forming lead sulphate, which will remain undissolved.

It is always less easy to dissolve a precipitate than to prevent its formation.]

*4. With potassium chromate they give a yellow precipitate.

This has been already shown, p. 346.

*5. Reduced before the blowpipe on charcoal they yield a malleable bead, and yellow incrustation.

Mix a little lead acetate with about twice as much potassium cyanide, and heat the mixture on charcoal as directed in expt. 2, p. 103. A metallic bead will be obtained, the malleability of which should be tested as there directed; and the surrounding parts of the charcoal will be covered with a light yellowish incrustation of lead oxide.

Additional Experiments.

1. Action of water on lead.

Fill two test-tubes, one half-full of distilled water, the other half-

¹ This may be made, if none is at hand, by putting about 3 c.c. of solution of ammonia into a test-tube, and adding hydrogen acetate until the liquid smells of it and is acid to test-paper.

If the solutions are made of the strengths indicated in Appendix B. I, you have simply to mix *equal volumes* of each, as explained at the beginning of that Appendix.

full of common hard spring water¹, and immerse in each a strip of lead, cleaned by scraping it with a knife. After the lapse of an hour or less, a slight white precipitate will be formed in the test-tube containing the distilled water, and in the course of a day some quantity of this precipitate will have been collected; while in the test-tube containing the common hard water there will be little or no perceptible action.

The reason is this:—The oxygen dissolved in the water attacks the lead, forming lead oxide, which (like calcium oxide, p. 66) combines with water, forming lead hydrate. This latter dissolves in the water, but is to some extent precipitated as carbonate by its combination with the carbon dioxide present in water. If, however, the water contains sulphates and carbonates (as common hard water does, p. 75), these form a crust of insoluble lead sulphate and carbonate which protect the lead from corrosion.

The presence of lead in solution in the test-tube containing the distilled water should be proved by applying to it test 2, p. 347.

2. Precipitation of lead from its compounds by zinc.

This depends upon the superior affinity of zinc for the radicle combined with the lead; and the action, once begun, is aided by the galvanic current set up between the zinc and the portions of lead first thrown down (compare the reduction of silver by zinc, p. 320).

Make a solution of lead acetate by dissolving 10 grms. of the salt in 200 c.c. of water; with addition of a few drops of hydrogen acetate. Place the filtered solution in a wide-mouthed bottle (a small gas bottle will do), and suspend in it, a strip of thick sheet zinc, or, better, a rod of the metal about as large as a pencil². A short piece of glass tubing should be laid across the mouth of the bottle, from which the zinc may be suspended by a piece of string, so that it may not touch the bottom of the bottle. Leave the whole undisturbed for twelve or fourteen hours: the rod of zinc will soon be covered with thin brilliant plates of pure metallic lead (the so-called 'Lead Tree'), while a proportional quantity of zinc is dissolved. This is a good illustration of the replacement of one metal by another in a combination; and, if we ascertained the weight of zinc

¹ If none of this is at hand, add 1 c.c. of solution of calcium sulphate to 10 c.c. of rain water and use it in the expt.

² As the shape of the rod is immaterial, it may be easily made by melting some zinc in a ladle, and casting it in a shallow trough formed by pressing a thick pencil or a piece of glass tube into a mass of fine slightly-moistened sand, or clay; or it may be cast in a groove cut in a piece of soft brick.

dissolved and the weight of lead deposited, we should find that the former weight was to the latter as 65 : 207, numbers which are the accepted weights of the atoms of zinc and lead respectively.

In a day or two the whole of the lead will have been withdrawn from the solution, which may then be examined by test 3, p. 348, to prove the absence of lead.

Group II.

Metals which are separated from solutions containing hydrogen chloride by hydrogen sulphide.

MERCURY (divalent), LEAD, COPPER, CADMIUM, BISMUTH,
ARSENIC, ANTIMONY, TIN, GOLD, PLATINUM.

1. COPPER.

[Symbol of atom, Cu (cuprum).]

Weight „ 63.5 hydrogen-atoms.]

[If any of the ordinary ores of copper, such as Copper Pyrites (copper-iron sulphide) and Malachite (copper carbonate) are at hand, their general characters should be noted, and after the tests for compounds of copper have been learnt, the minerals may be examined to prove that they contain the metal. The process of copper smelting is a rather complicated one: the principles of it should be carefully studied in a text-book.]

Preparation of Compounds of Copper.

	Formula of molecule.
[Typical examples,—Copper oxide,	CuO
„ nitrate,	Cu(NO ₃) ₂
„ sulphate,	CuSO ₄]

1. Copper nitrate.

Dissolve 1 gm. of fine copper wire in about 5 c.c. of strong hydrogen nitrate diluted with half its volume of water, heating the tube gently if the action becomes slow. Red vapours of nitrogen tetroxide will be seen above the liquid (the chemical action has been already explained, p. 172), and a blue solution of copper nitrate will be obtained. Pour nearly all the solution

into a small dish, reserving five or six drops for use in expt. 2 *c*, and evaporate it to perfect dryness. The residue will be wanted for use in expt. 2 *b*.

2. Copper oxide.

(a) By the direct combination of oxygen with copper, when heated.

Clean a strip of sheet copper with emery paper, and hold it in the upper part of the flame of a Bunsen's burner. As it gets hot, brilliant-coloured films of copper oxide will form on it, where it is exposed to the current of hot air rising with the flame¹. Finally, when it has been heated to redness for a minute (best in the flame of a Herapath's blowpipe, or in a fire), so as to form a thick black coating of the oxide, plunge it into a beaker of cold water, when the oxide will detach itself in scales (since it does not contract, as the temperature falls, in the same degree as the metal), and the surface of the metal will show the characteristic red colour of copper.

(b) By the decomposition of copper nitrate by heat.

Take the dish containing the residue of copper nitrate obtained in expt. 1, and heat it over a Bunsen's burner, gently at first (moving it about in the flame lest it should crack), and finally as strongly as possible. Orange vapours of nitrogen tetroxide will be given off, together with some oxygen, and a black residue of copper oxide will be left. The reaction is quite analogous to the decomposition of lead nitrate (p. 167) and mercury nitrate (p. 337) under similar circumstances.

(c) By gently heating copper hydrate.

Take the remainder of the solution of copper nitrate obtained in expt. 1, dilute it with a little water, and add excess of solution of potassium hydrate. A light blue precipitate of

¹ Observe that not only does the part of the copper which is actually immersed in the flame remain bright, but when the blackened part is brought into the middle of the flame the oxide is reduced and the bright red metal reappears. In fact, by holding the strip edgewise in the flame we get a good section of the oxidising and reducing parts.

The iridescence of the films of copper oxide which are first formed is due to the interference of the rays of light reflected from the upper and under surfaces of the film respectively: due to the same cause, in fact, as the colours of a soap bubble.

copper hydrate (CuH_2O_2) will be produced. Now heat the contents of the tube to boiling; the precipitate will turn black, being decomposed into copper oxide and water¹.

3. Copper sulphate ('blue vitriol').

A method of preparing this, the commonest and most important salt of copper, has been described already, p. 288. A solution of the salt will be wanted in several of the following expts., and should be made by dissolving 2.5 grms. of it in 40 c.c. of water, and diluting to 50 c.c.

Reduction of compounds of Copper.

1. Reduction of copper oxide to the suboxide.

Copper, like mercury, forms a series of compounds in which its atom is only monovalent. These, which are known by the name of 'sub-salts,' are comparatively unimportant; and the suboxide (Cu_2O) is the only one which will be noticed here. It is made by taking away from two molecules of the oxide (2CuO , or Cu_2O_2) one-half the oxygen they contain, and grape sugar is the most convenient reducing agent for the purpose.

Dissolve a small lump (about the size of a pea) of grape sugar in 5 c.c. of water; filter the liquid, if necessary, and add to it a drop or two of the solution of copper sulphate. If solution of potassium hydrate be now added, no precipitate of copper hydrate will be formed, or if formed (owing to the grape sugar not being present in sufficient quantity) it will be redissolved on addition of more potassium hydrate. The reason is that grape sugar forms a soluble compound with copper hydrate (the exact nature of which, however, has not yet been made out with certainty).

Now heat the clear dark-blue fluid gradually to boiling; a yellow precipitate will soon appear, consisting of copper subhydrate (CuHO); and this, as the temperature approaches the boiling-point, will turn red, being decomposed into copper suboxide and water².

¹ $\text{Cu H}_2\text{O}_2 = \text{CuO} + \text{H}_2\text{O}$

² $2 \text{Cu HO} = \text{Cu}_2\text{O} + \text{H}_2\text{O}$

The reducing action of the grape sugar is due (as in the case of the tartarates, p. 323) to the carbon and hydrogen in it; both of these take from the copper hydrate part of the oxygen it contains.

2. Reduction of copper oxide to metallic copper.

All organic substances effect this when strongly heated with it; in fact, the usual process of analysis of an organic substance (such as sugar, wax, acetates, tartarates, &c.) consists in heating to redness a known weight of the substance with copper oxide. The oxygen of the latter unites with the carbon and hydrogen of the substance to form carbon dioxide and water, which are collected and weighed. The principle of the process may be illustrated on a small scale as follows.

(a) Mix a small quantity of copper oxide (as much as will lie on the end of a spatula) intimately with about an equal quantity of sodium acetate in a mortar; fill the bulb of an ignition-tube with the mixture and heat it, gently at first, finally to redness. Carbon dioxide and water will be given off, and a residue of metallic copper, recognised by its dull red colour, will remain in the bulb.

(b) Place a small quantity of copper oxide in the bend of a tube shaped like that shown in fig. 91, p. 343: connect the longer branch of the tube with the gas-supply; pass a gentle stream of coal-gas over the oxide, and heat the latter to low redness. It will glow brightly as its oxygen unites with the carbon and hydrogen of the gas. Allow the tube to cool (continuing a slow stream of gas until the temperature falls decidedly below redness): the red powder of metallic copper may then be shaken out and examined.

3. Reduction of copper sulphate by iron, with formation of metallic copper.

Pour a little of the solution of copper sulphate into a test-tube, and dip into it a strip of sheet iron cleaned with emery paper, or the blade of a knife. Metallic copper will be thrown down on the surface of the iron, while the latter is slowly dissolved, taking the place of the copper in the solution. Compare the action of zinc on lead acetate, p. 349.

4. Reduction of copper salts by electricity.

Copper is one of the metals most easily reduced by electricity, and an experiment illustrating this has already been made, p. 79. An account of the process of electrotyping, which is now applied to very numerous purposes¹, is given on p. 355.

Tests for Salts of Copper.

[The solution of copper sulphate, already made, can be used.]

***1. Their solutions, when mixed with hydrogen sulphide, give a black precipitate, insoluble in dilute acids and in potassium hydrate.**

Acidify a portion of the solution of copper sulphate with hydrogen chloride, and add solution of hydrogen sulphide. A black precipitate will be formed, consisting of copper sulphide, which is insoluble in the excess of hydrogen chloride present. Add to it excess of solution of potassium hydrate, and warm it. The precipitate will remain undissolved: this distinguishes it from the black sulphides of tin, gold, and platinum, which dissolve under similar circumstances.

***2. With potassium ferrocyanide they give a reddish-brown precipitate.**

This should be tried with only one drop of the solution of copper sulphate, diluted with 5 c.c. of water, in order that the delicacy of the test may be observed.

***3. With ammonia they give a light blue precipitate, soluble in excess, forming a blue solution.**

To another portion add one drop of solution of ammonia. A light blue precipitate will be formed of copper hydrate, which will readily dissolve on addition of a few more drops of ammonia, and a deep blue solution will be obtained. This contains cuprammonium sulphate, a salt in which part of the hydrogen in the radicle ammonium is replaced by copper, as shown in its formula $(H_4CuN_2)SO_4$.

¹ All the engravings in this book are printed from electrotype copies of the original wood-cuts, and not from the box-wood blocks themselves. Many books are now printed, not from the type, but from copper 'stereotype' plates, produced by the electrotype process.

4. They impart, when volatilised, a green colour to flame.

Put a drop or two of strong hydrogen chloride into a watch-glass, dip into it the end of a piece of copper wire, and hold the latter in the flame of a Bunsen's burner. The copper chloride which has been formed will volatilise in the flame and give it a bright bluish green colour.

*5. Heated with borax, they give a bead which is greenish-blue in the oxidising flame, red and opaque in the reducing flame.

Make a borax bead, add to it a trace of copper sulphate, and heat it in the oxidising flame of the blowpipe. The bead will be coloured green while hot, becoming blue as it cools. After being heated in the reducing flame, with addition of a little more copper sulphate, it will appear red by reflected light, owing to the presence of suspended particles of copper.

6. Heated on charcoal with potassium cyanide they give grains of metallic copper.

Mix a minute quantity of copper sulphate with about as much potassium cyanide, and heat it on charcoal before the blowpipe flame. You will obtain small grains of metallic copper, but the heat of the blowpipe flame will be scarcely sufficient to fuse these into one globule. They will be better seen if the fused mass is placed in a mortar and washed with water until the soluble salts are dissolved; the red metallic particles may then be readily distinguished with a magnifier.

Additional Experiment.

Method of obtaining Electrotypes.

When a current of electricity is sent through a solution of a salt of copper, the metal is deposited upon the negative electrode (i.e. upon that which is connected with the zinc plate of the battery), and since it is deposited molecule by molecule, the particles form a film which adheres very closely to, and is an exact copy of, the electrode itself. In order, therefore, to obtain a copy of a seal or medal, a 'mould' or reversed impression must be first obtained, which is placed as the negative electrode in a solution of copper

sulphate, and the current is kept up until a sufficiently thick film of copper is deposited.

To obtain the current it will not be necessary to employ a separate battery. A 'single-cell' apparatus, arranged as directed below, will answer perfectly: the mould itself forming the negative plate of the battery¹.

[Solutions required:—

Saturated solution of copper sulphate (250 grms. of the salt dissolved in 1 litre of water; 20 c.c. of hydrogen sulphate added).

Solution of ammonium chloride (60 grms. dissolved in 300 c.c. of water).

If the zinc is amalgamated (see under ZINC), it is preferable to use dilute hydrogen sulphate (20 c.c. of the strong acid mixed with 250 c.c. of water) instead of the above solution of ammonium chloride.]

1. Preparation of the mould.

For seals nothing is better than good sealing-wax. Some of this should be melted on a card held at some height above a lamp-flame, and continually stirred with the end of the stick of wax until sufficient has been melted to form a thick circular lump rather smaller than the seal to be copied. After breathing upon the seal, bring it down with gentle pressure upon the wax, increasing the pressure as the wax gets cold and hard. It is best not to remove the seal until the wax is quite hard, otherwise the mould may lose its flatness. The card should next be cut away carefully close to the edges of the wax, and a copper wire (about No. 20 wire-gauge) 30 cm. long should be attached to the margin of the mould by heating it and pressing it into the wax near (but not touching) the edge of the impression. The wire must not be completely buried in the wax, and the exposed part should be scraped clean with a knife.

For a medal, plaster of Paris will answer very well, and the mould may be made according to the directions given under CALCIUM, being thoroughly saturated with wax in the manner there described. The end of a piece of copper wire, about 40 cm. long, should be passed round the rim and fastened by twisting to the main portion of the wire, so as to grasp the mould securely in a loop.

Since wax is a non-conductor of electricity the surface of the

¹ For a fuller explanation of the principles of electrolysis a text-book on Electricity must be consulted.

mould must be rendered conductive by covering it with a thin film of graphite (the ordinary plumbago or black-lead). For this purpose it should be laid face upwards on a sheet of paper and brushed over with some of the best plumbago¹: being lightly breathed upon occasionally to promote the adhesion of the substance. If the plumbago does not adhere well, hold the face of the mould, for a few seconds only, just over the surface of a little alcohol (previously warmed) placed in a watch-glass. The vapour will soften the wax and enable the plumbago to stick to it. The brush should be worked with quick circular strokes into all the crevices of the mould, until every part of it shows a metallic lustre when looked at obliquely. An extremely thin film is all that is required, but it must be continuous. A little plumbago must be brushed over the wire where it is attached to the mould, to make a good connexion throughout. Lastly, the edges of the mould outside the wire, and about 10 or 12 cm. of the wire itself, must be varnished with 'black japan' or some other thick varnish², to prevent the deposition of copper upon them when immersed in the solution.

[If the mould is of fusible metal (see p. 362) a portion of its edge should be moistened with solution of ammonium chloride and a clean piece of copper wire heated and pressed against it until completely imbedded. The back and edges of the mould must be thickly varnished to prevent deposit of metal upon them; and it is advisable to brush a trace of black-lead over the impression to prevent too close adhesion of the deposit.]

2. Construction of the apparatus.

Place a small jar of porous earthenware about 14 or 15 cm. high and 4 cm. in diameter in a wider jar of glass or china about 11 or 12 cm. in diameter and the same or rather more in height³. Put into the porous cell a rod of zinc about 18 or 20 cm. long, and at

¹ Good stove black-lead will generally serve the purpose; but it is best to obtain a little pure plumbago from a chemist or optician. A soft tooth brush or plate brush answers well for applying it.

² Sealing-wax varnish may be made by powdering 10 grms. of black sealing-wax, and digesting it at a gentle heat (best applied by a pan of hot water) with 10 c.c. of methylated spirit, stirring occasionally.

³ For the porous cell, a common flower-pot, though unnecessarily wide, answers well, the hole at the bottom being stopped with a cork.

For the wider jar nothing is better than the lower part of a large common green glass bottle, the neck being cut off by the method given on p. 42.

A preserve jar or gallipot will answer, but the solution is apt to penetrate the glaze, unless the material is stoneware.

least as thick as a pencil¹. Hang the mould in the outer jar by bending the wire round the rim of the jar as shown in fig. 92, the

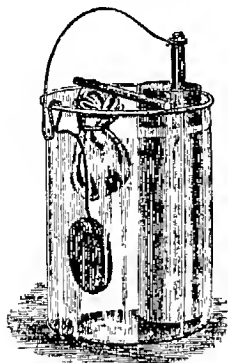



Fig. 92.

bend being made thus:  otherwise the solution may creep up between the wire and the side by capillary action, and overflow. The other end of the wire should be twisted firmly round the zinc rod, so as to support it in the porous cell.

Lastly, fill the porous cell about three-fourths full of the solution of ammonium chloride (or, if the zinc is amalgamated, of dilute hydrogen sulphate)², and the outer jar to the same level with the solution of copper sulphate.

In the course of a minute a bright deposit of copper will be seen spreading over the mould. If it does not appear, there must be a break in the conducting surface, and the mould must at once be taken out, dried, and blacklead with more care. When all is going on well, hang a small muslin bag containing crystals of copper sulphate just below the top of the solution in the outer jar, tying it to a glass rod laid across the jar: and leave the whole undisturbed for about a day, examining it occasionally to see that the deposit is forming regularly on the mould. The latter should not, however, remain out of the solution for more than half a minute, lest it should tarnish and the subsequent deposit fail to adhere to it³.

The defects which are most liable to occur are—

1. *Gas given off at the surface of the mould, and a sandy, dull-red, non-adherent deposit of metal.*

This is caused by the current being too strong in proportion to the strength of the copper sulphate solution. The remedy will

¹ This may be cast in the manner described on p. 349, note.

² If the mould is small, it will be advisable to use a much weaker solution of ammonium chloride (or acid) (the strong solution diluted with an equal volume of water), at any rate for the first half-hour, or until the impression is completely covered with copper.

³ A black deposit forms upon the zinc, and should be occasionally brushed off. It consists of copper, and is due to the copper sulphate slowly diffusing into the porous cell, and being reduced by the zinc.

be to pour off about two-thirds of the solution of ammonium chloride (or acid) in the porous cell and add an equal volume of plain water to the remainder. The solution of copper sulphate must be kept fully saturated, fresh crystals being placed in the bag as the others dissolve.

2. *The deposit forms very slowly; its surface being rough and bristling with crystals of copper.*

This is due to the current of electricity not being strong enough; the action of the solution of ammonium chloride on the zinc having slackened. The spent solution must be poured away, and the porous cell filled up with fresh solution of the same salt (or acid). The same deficient action occurs in cold weather, and the apparatus should be kept in a warm room.

When the conditions are right, the deposit appears of a bright pink colour, with an even surface, and tough in texture.

In about 24 hours a sufficiently thick film of metal will have been deposited, and the mould may be taken out and the copy detached from it by pulling the two apart very carefully. If there is much difficulty in separating them, the point of a knife may be inserted at the edges, and the copper film heated for a moment over a lamp.

The thin, fragile deposit should next be strengthened by backing it up with tin. To do this, moisten the back of it with solution of ammonium chloride, lay it face downwards on a piece of wire-gauze, and heat it over a lamp. When the ammonium chloride begins to volatilise in white fumes, press upon the surface the end of a strip of metallic tin (or, better, soft solder). This will melt and spread all over the copper; enough should be applied to make a layer at least 1 mm. thick.

Lastly, the edges should be trimmed by cutting away all superfluous copper, and smoothing irregularities with a file.

If the object is a medal, an electrotype of each side may be taken, and the two placed back to back and soldered together (or simply cemented by shellac) so as to reproduce the original.

If a copy of a seal has been taken, it may be soldered to the head of a brass screw, and the latter inserted into a wooden handle such as those which are sold for bradawls.

[A rather preferable method of depositing copper is to employ a separate battery, such as a single cell of Smee's battery; the mould being connected with the zinc, and a thick strip of copper with the platinised silver of the battery. Both should then be immersed in a jar containing a solution of copper sulphate (150 grms.

dissolved in 1 litre of water; 30 c.c. of hydrogen sulphate added). No addition of crystals of copper sulphate should be made: the copper being dissolved from the positive electrode (the strip of copper) as fast as it is deposited on the negative electrode (the mould).]

2. CADMIUM.

[Symbol of atom, Cd.

Weight „ 112 hydrogen-atoms.]

This metal much resembles zinc in its physical, though not in its chemical, properties. It is, however, more volatile than zinc; and if any of it is at hand, its volatility may be proved by heating a small fragment in an ignition-tube to full redness. A portion of the metal, as it becomes vapour, will combine with the oxygen of the air in the bulb and form a reddish-brown sublimate of cadmium oxide in the tube, but below this bright drops of metallic cadmium will condense, as the heat is continued and increased.

Owing to this volatility the density of cadmium vapour has been determined, and hence the weight of the molecule of cadmium is known with more certainty than in the case of the great majority of metals.

Compounds of Cadmium.

	Formula of molecule
[Typical examples,—Cadmium oxide,	CdO
„ sulphide,	CdS
„ sulphate,	CdSO ₄]

[In some of the following experiments a solution of cadmium sulphate, containing 1 grm. of the salt in 25 c.c. of water, will be required.]

Preparation of Cadmium sulphide.

Add to a portion of the solution of cadmium sulphate some solution of hydrogen sulphide. A bright yellow precipitate of cadmium sulphide will be produced, which is used as a paint, and has the advantage of great permanency; not being, for

instance, blackened by sulphides, like lead chromate, or volatile, like arsenic sulphide.

[Keep the contents of the test-tube for further examination.]

Tests for Salts of Cadmium.

*1. Their solutions, when tested with hydrogen sulphide, give a yellow precipitate, insoluble in potassium hydrate and ammonium sulphide.

Add to the yellow precipitate obtained in the last expt. excess of solution of potassium hydrate, and warm the mixture. The precipitate will remain unaltered, differing in this respect from the two other yellow metal-sulphides, those of arsenic and tin, which are dissolved under the same circumstances.

*2. With ammonia they give a white precipitate, soluble in excess; this solution yields a yellow precipitate on addition of hydrogen sulphide.

Add a drop of ammonia to a portion of the solution of cadmium sulphate. A white precipitate of cadmium hydrate will be formed, which will readily dissolve on addition of more ammonia. Add to the clear solution some hydrogen sulphide. A yellow precipitate will be formed, of cadmium sulphide, since the latter is insoluble in ammonia and ammonium sulphide.

*3. Reduced on charcoal they give a reddish-brown incrustation.

Mix a small quantity of cadmium sulphate with an equal amount of potassium cyanide, and heat it on charcoal before the blowpipe. No metallic globule will be obtained, owing to the volatility of cadmium, but the surface of the charcoal will be covered with a characteristic reddish-brown coating of cadmium oxide.

3. BISMUTH.

[Symbol of atom, Bi.

Weight „ 210 hydrogen-atoms.]

Bismuth is, unlike most metals, very brittle and easily crushed. Place a small piece of bismuth in a strong porcelain mortar,

and strike it with the pestle. It will not spread out, as lead does, into a thin plate, but will break into fragments. Notice the crystalline structure of the freshly-broken surfaces, and then grind about 1 grm. of the metal to fine powder for use in a future experiment.

Preparation of 'Fusible metal.'

Although bismuth itself only melts at a temperature of 260° , yet an alloy of it with tin (melting-point 230°) and lead (melting-point 330°) fuses below the temperature of boiling water, viz. at 98° .

Weigh out 4 grms. of bismuth, 2 grms. of lead, and 2 grms. of tin. Melt the bismuth in a clean iron spoon, and add to it the lead and the tin, stirring the melted alloy with a glass rod or piece of iron wire. Pour it out on a clean iron plate or on a tile, and allow it to cool.

Meanwhile, heat some water in a large test-tube, and when it is boiling put into it a piece of the alloy suspended in a loop of thread. It will readily melt, and drop off the thread.

A still more fusible alloy is made by adding 1 grm. of cadmium to the above ingredients. This melts at a temperature of 80° , or a little below.

[Since the above alloy expands in solidifying, it is well adapted for taking casts of seals, medals, &c., for electrotyping. For this purpose, some of it should be melted and poured out on a clean plate. The edge of a card should be lightly drawn over its surface, to remove dross, and the moment it is observed to become pasty the seal should be brought down quickly upon it. A little practice will be required to hit the exact moment for applying the seal.]

Preparation of Compounds of Bismuth.

	Formula of molecule.
[Typical examples,—Bismuth nitrate,	$\text{Bi}(\text{NO}_3)_3$
„ basic nitrate,	$\text{BiH}_2\text{O}_2(\text{NO}_3)$
„ chloride,	BiCl_3
„ basic chloride,	BiOCl

1. Bismuth nitrate.

Dissolve 1 grm. of finely-powdered bismuth in 5 c.c. of

hydrogen nitrate diluted with 2 c.c. of water. The chemical action is similar to that which occurs in the case of copper, already explained.* When the metal has dissolved, which it will readily do, add an equal volume (not more) of water and keep the solution for experiments.

2. Bismuth basic nitrate.

Most salts of bismuth are readily acted on by water with formation of 'basic salts'; the general character of the action being that the hydrogen of the water withdraws some of the electro-negative radicle (e.g. the nitrate), while the oxygen of the water takes the place of this radicle in the salt. The result of this withdrawal of part of the 'acid' radicle is to cause a preponderance of the 'basic' or metallic radicle in the compound: hence the name by which such salts are usually known.

Pour six or eight drops of the solution of bismuth nitrate into a test-tube, and add eight or ten times its volume of water. The solution will gradually become cloudy, and deposit a white precipitate of bismuth basic nitrate¹.

This salt, under the name of 'subnitrate' or 'oxynitrate' of bismuth, is of some importance in medicine and as a paint.

[If the solution of bismuth nitrate contains a great excess of acid, the decomposition is delayed or prevented. In this case it will be best to evaporate a little of the solution to half its bulk, and then add water as above directed.]

3. Bismuth basic chloride (or 'oxychloride').

Bismuth chloride (which is readily formed by the addition of hydrogen chloride to a salt of bismuth) is much more easily decomposed by water than the nitrate: and the reaction forms a very characteristic test for the presence of bismuth in a solution.

To another small portion of the solution add one drop of dilute hydrogen chloride, and then a large quantity of water, as above.

¹ $\text{Bi}(\text{NO}_3)_3 + 2 \text{H}_2\text{O} = \text{BiH}_2\text{O}_2(\text{NO}_3) + 2 \text{HNO}_3$

It is to be observed that some of the hydrogen of the water, as well as the oxygen, takes a place in the basic salt.

The liquid will at once turn milky, owing to the formation of bismuth oxychloride¹.

[Reserve the contents of the tube for further examination.]

Tests for compounds of Bismuth.

***1.** Their solutions, when mixed with hydrogen chloride and diluted with water, give a white precipitate, soluble in excess of acid, but insoluble in tartrates.

Take the test-tube containing the precipitate of bismuth basic chloride, obtained in the last experiment, shake up the precipitate if it has subsided, and pour half of the mixture into another tube:—

(a) To one portion add strong hydrogen chloride drop by drop. The precipitate will readily dissolve. [Reserve the solution for test 2.]

(b) To the other add an equal volume of solution of sodium-hydrogen tartrate. The precipitate will remain undissolved: a property which distinguishes it from the similar precipitate formed by antimony, p. 376.

[The best method of applying this test is, to evaporate a few drops of the solution of the bismuth salt to dryness in a watch-glass, to dissolve the residue in one drop (not more) of moderately dilute hydrogen chloride, and then, placing the watch-glass on a black surface, to fill it up with water from a wash-bottle. A very slight turbidity may thus be rendered evident.]

***2.** With hydrogen sulphide they give a black precipitate, insoluble in potassium hydrate.

Add solution of hydrogen sulphide to the clear solution containing bismuth chloride, obtained in the last experiment. A black precipitate of bismuth sulphide will be produced, insoluble in potassium hydrate.

***3.** Reduced on charcoal they give a brittle globule of metal, with a light yellow incrustation.

Evaporate the remainder of the solution of bismuth nitrate to

¹ $\text{BiCl}_3 + \text{H}_2\text{O} = \text{BiOCl} + 2\text{HCl}$

dryness, mix the residue with about an equal quantity of sodium carbonate, and reduce it on charcoal in the usual way, remembering that nitrates deflagrate on charcoal, and hence heat must be applied cautiously. Observe the yellow incrustation of bismuth trioxide formed round the cavity in the charcoal, and try the brittleness of the globule by crushing it with the pestle in the mortar.

4. ARSENIC.

[Symbol of atom, As.

Weight „ 75 hydrogen-atoms.]

[It should be remembered in dealing with arsenic that the substance and its compounds are extremely poisonous. Very small quantities should be used for testing, and care must be taken not to inhale any of the vapours.]

Arsenic is remarkable as not only forming salts in which it acts as a metal, but also entering into compounds as part of the non-metallic radicle; showing, in fact, analogies to bismuth on the one hand and nitrogen on the other.

It occurs in many metal-ores, especially in some kinds of pyrites; and its most important compound, arsenic trioxide, is chiefly obtained during the process of roasting these ores.

If any mispickel (arsenical pyrites) is at hand, the process may be illustrated as follows.

Grind a small fragment of the mineral to very fine powder, and place a little of it in the bend of a roasting-tube (fig. 91, p. 343). Warm the long branch of the tube to establish an upward current of air in it, and then heat the powder in the bend very slowly and gently. A white crystalline sublimate of arsenic trioxide will form in the tube, the oxygen of the heated air having combined with the arsenic in the mineral. If the heat is at all too great, or too rapidly applied, a yellow sublimate of arsenic trisulphide and possibly black shining crystals of metallic arsenic will appear.

A. Compounds in which Arsenic acts as a metal.

	Formula of molecule.
[Typical examples,—Arsenic trioxide,	As_2O_3
„ pentoxide,	As_2O_5
„ trisulphide,	As_2S_3
„ trichloride,	AsCl_3

1. Arsenic trioxide.

This is the common 'white arsenic' of the shops, and is the source from which other compounds of arsenic are usually derived. The process by which it is manufactured has been alluded to above; the following characteristic properties of it should be examined.

*(a) It volatilises readily, condensing in brilliant octohedral crystals.

Place a very small quantity of arsenic trioxide in a small dry test-tube, and heat it slowly over a lamp with a small flame. It will volatilise completely, forming a crystalline crust in the cool part of the tube. Now warm the part of the tube beyond the deposit, and when it is moderately hot carry the lamp flame downwards, so as to volatilise the sublimate already formed. It will now condense more slowly,



Fig. 93.

and form large transparent glittering crystals, which, when examined with a magnifier, will be found to resemble fig. 93, being more or less perfect octohedra belonging to the 'regular' or 'monometric' system. The triangular faces of these will be easily recognised.

(b) It is slightly soluble in water.

Boil a very little of it in a test-tube with 8 or 10 c.c. of water; notice the difficulty with which it is wetted by the water, the powder showing a tendency to float as a film upon the surface of the liquid, or remain at the bottom in lumps. It will,

however, dissolve to a certain extent, as may be proved by setting the liquid aside to cool, when small brilliant crystals of the trioxide will be formed on the sides of the tube. The solution may be shown to contain arsenic by test 1, p. 372.

2. Arsenic trichloride.

Boil half a gramme of arsenic trioxide with 5 c.c. of strong hydrogen chloride in a test-tube. The substance will readily dissolve¹, and the solution, which contains arsenic trichloride, may be kept for examination.

3. Arsenic trisulphide ('orpiment').

Add a few drops of the solution of arsenic trichloride to 5 c.c. of water, and then some solution of hydrogen sulphide. A bright yellow precipitate of arsenic trisulphide (the common 'orpiment' used as a paint) will be formed.

[Keep the contents of the tube for further examination.]

B. Compounds in which Arsenic forms part of, or acts as, a non-metallic radicle.

	Formula of molecule.
[Typical examples,—Potassium arsenite,	K AsO_2
Copper „	Cu HAsO_3
Ammonium thioarsenite,	$(\text{H}_4\text{N}) \text{AsS}_2$
Hydrogen arsenate,	H_3AsO_4
Potassium arsenate,	K_3AsO_4
Hydrogen arsenide,	H_3As

In these arsenic shows decided analogies to nitrogen and phosphorus; the arsenites corresponding to the nitrites and phosphites, and the arsenates to the phosphates; while hydrogen arsenide resembles ammonia (H_3N) and hydrogen phosphide (H_3P) in many points besides the structure of its molecule.

1. Potassium arsenite.

Boil 1 grm. of arsenic trioxide with 5 c.c. of solution of potassium hydrate. An action will take place exactly similar to that between nitrogen trioxide and potassium hydrate (p. 168),



and a solution of potassium arsenite will be soon formed¹, which should be kept for future experiments.

2. Copper arsenite ('Scheele's green'):

Mix a little of the solution of potassium arsenite with about 5 c.c. of water and add a few drops of solution of copper sulphate. A grass-green precipitate of copper arsenite will be formed. This is the brilliant but very poisonous paint called 'Scheele's green.'

3. Ammonium thioarsenite (or sulpharsenite).

Just as arsenic trioxide acts upon potassium hydrate (as shown in the last expt. but one) to form potassium arsenite, so arsenic trisulphide will combine with potassium sulphide or ammonium sulphide and form a salt called a, 'thioarsenite' (analogous to an arsenite but containing sulphur in place of oxygen, as seen by comparison of the formulae in the list above given). In illustration of this—

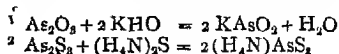
Take the tube containing the arsenic trisulphide already prepared (expt. 3, p. 367), add sufficient ammonia to neutralise the free acid in it, and then add a few drops of solution of ammonium sulphide and warm the mixture. The arsenic trisulphide will dissolve, since ammonium thioarsenite is soluble in water².

A similar result occurs when potassium hydrate is used; a mixture of potassium arsenite and thioarsenite being formed.

This illustrates a method used in analysis for distinguishing and separating arsenic sulphide from cadmium sulphide; the latter being unaltered when similarly treated.

4. Hydrogen arsenate, and Potassium arsenate.

Arsenic trioxide shows a tendency to combine with more oxygen, like nitrogen trioxide and phosphorus trioxide; though it will not, like the latter, combine with oxygen directly. Hydrogen nitrate readily effects the change, and the pentoxide when formed combines with the elements of water to produce hydrogen arsenate (corresponding to hydrogen orthophosphate).



(a) Place half a gramme of arsenic trioxide in a small evaporating dish, pour over it about 5 c.c. of strong hydrogen nitrate, and heat the mixture (in a draught-cupboard, if possible). Orange vapours of nitrogen trioxide will be evolved, some of the oxygen of the acid being transferred to the arsenic trioxide¹. When the liquid has nearly evaporated, add about 2 c.c. more acid and evaporate to complete dryness. Use the residue of hydrogen arsenate for the next experiment.

(b) Boil the residue, obtained above, with about 5 c.c. of solution of potassium hydrate, dilute the solution of potassium arsenate, thus obtained, with 20 c.c. of water, and reserve it for testing, p. 373.

5. Hydrogen arsenide.

This is obtained whenever hydrogen in the nascent state is brought into contact with arsenic or a compound of it; just as ammonia was formed from a nitrate under similar conditions (p. 165). The hydrogen may be obtained, as already seen, by the action of zinc on either an acid or an alkali.

[Hydrogen arsenide is a very poisonous gas, and the contents of the test-tubes used in the following expts. should be washed away as soon as possible.]

(a) Place a little dilute hydrogen sulphate in a test-tube and drop in a bit of pure granulated zinc². Hydrogen will, of course, be given off and should be allowed to fill the tube. Place on the mouth of the tube a small bit of white blotting-paper moistened with solution of silver nitrate. No discolouration of the paper will be produced, if the zinc and acid are pure (see note below²). Now put in one drop of the solution of arsenic trichloride, on a glass rod, and stir it up. The evolution of gas will be much increased, hydrogen arsenide being given off mixed with the hydrogen. The following properties of the gas should be observed.

¹ $\text{As}_2\text{O}_3 + 2 \text{HNO}_3 + 2 \text{H}_2\text{O} = \text{N}_2\text{O}_5 + 2 \text{H}_3\text{AsO}_4$

² Common granulated zinc often contains arsenic and is unfit for these experiments. The metal of the thin rolled sheets is, however, usually sufficiently pure. Common hydrogen sulphate also may contain arsenic, and should not be used.

Its offensive smell.

This should be observed cautiously, as the gas is extremely poisonous.

Its power of reducing silver salts.

Place the strip of blotting-paper moistened with silver nitrate upon the mouth of the test-tube. It will turn black, owing to formation of metallic silver.

[Other properties of the substance will be found under 'Marsh's test,' p. 379, the principle of which test is illustrated by the above experiment.]

(b) Put a little solution of potassium hydrate into a test-tube, add a bit of granulated zinc and a drop of solution of arsenic trichloride, and boil the mixture. Hydrogen arsenide will be given off, as in the last expt., and for a similar reason; its presence may be proved by the blackening of a slip of blotting-paper moistened with silver nitrate.

This experiment illustrates 'Fleitmann's test' for arsenic, a very simple and reliable one.

Methods of reduction of compounds of Arsenic.**1. By heating with sodium carbonate and potassium cyanide.**

Mix a very small quantity of arsenic trioxide with the same amount of potassium cyanide and about twice as much anhydrous sodium carbonate. Half-fill the bulb of an ignition-tube with the mixture, and wipe off any adhering particles from the

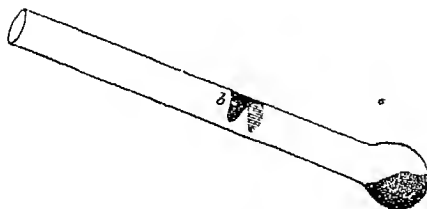


Fig. 94.

sides of the tube with a twisted strip of blotting-paper. Heat the bulb, gently at first, over the lamp, and warm the whole of the tube (held in the crucible tongs) so as to drive

out any moisture which would otherwise condense in it. When the whole is quite dry (the last portions of moisture may be

absorbed by a strip of blotting-paper, so as to leave the whole of the tube quite clean), heat the mixture in the bulb more strongly. A black, shining ring of metallic arsenic will soon form in the tube (fig. 94). Allow the whole to cool and then cut off the bulb with a file, retaining the metallic sublimate in the tube; hold the latter in a slanting position (the part containing the arsenic being lowest), and heat the ring, beginning at the upper part, by a lamp with a very small flame. The arsenic will volatilise, will be oxidised by the current of hot air ascending in the tube, and will condense near the top of the tube as arsenic trioxide, in small crystals. The heat should not be too strong, or a portion of the arsenic will volatilise unchanged and interfere with the distinctness of the crystalline ring. If this should occur, allow the tube to cool, and re-sublime the deposit, as above directed.

2. By heating with metallic copper, in presence of hydrogen chloride.

This is a case of the replacement of one metal by another which has more affinity for the non-metallic radicle present. Just as iron has been shown to replace copper (expt. 3, p. 353), so copper will replace arsenic in combination with chlorine: the arsenic being thrown down in the metallic state.

Pour about 5 c.c. of dilute hydrogen chloride into a test-tube, and add two or three drops (not more) of the solution of arsenic trichloride lately made. Put into the liquid a narrow strip of copper foil, 4 or 5 cm. long, or a piece of flattened copper wire, cleaned with emery paper, and doubled up into a bundle. On boiling the solution, a dark film of arsenic will be deposited on the copper, and will, if the action be continued, separate in scales from the copper. Decant the solution, and pour some fresh water upon the coated copper, to wash away the last traces of the solution; then shake the copper out of the tube upon a piece of blotting-paper and dry it by gentle pressure, taking care not to disturb the film of arsenic; complete the drying by gently warming the copper over a lamp-flame for a few seconds, then place it in an ignition-tube and draw out the middle of the latter in the blowpipe flame until it is

contracted like the tube represented in fig. 34, p. 32. When it is cool, heat the bulb containing the copper, and notice that a ring of crystals is deposited at the contracted portion, which may with a magnifier be easily recognised as octohedra of arsenic trioxide.

[This test, which is usually called 'Reinsch's test,' has the advantage that the presence of organic substances (*e.g.* milk, beer, in cases of poisoning) does not interfere with the deposition of arsenic on the copper. But other metals, such as antimony, bismuth, silver, are deposited on the copper under the same conditions as arsenic. Moreover, when the deposit of arsenic is heated, only a portion of the metal is volatilised, the rest forming a non-volatile alloy with the copper. The test, therefore, is by no means so reliable and characteristic as Marsh's test, which is described on p. 379.]

Tests for Arsenic protosalts and Arsenites.

[The solutions of arsenic trichloride and potassium arsenite, already made, may be used.]

***1.** Their solutions, tested with hydrogen sulphide, in presence of hydrogen chloride, give a yellow precipitate, soluble in ammonium sulphide and potassium hydrate.

The details of this test have been already given, pp. 367, 368.

***2.** With silver nitrate, their solutions, when neutral, give a yellow precipitate.

The following method of applying this test will illustrate a mode of ensuring absolute neutrality in some portion of a liquid under examination.

To a portion of the solution of potassium arsenite add enough dilute hydrogen nitrate to make the solution decidedly acid, and then add a drop of solution of silver nitrate.

[If the hydrogen nitrate or potassium arsenite contained any chloride, a slight white precipitate will form on addition of the silver nitrate, which should be filtered off.]

Mix in another test-tube some solution of ammonia with an

equal volume of water, and pour the diluted ammonia from a pipette very slowly and carefully down the side of the test-tube containing the arsenic solution, so that the two fluids may not mix, but the lighter solution (the ammonia) may rest on the surface of the heavier. The tube containing the arsenic solution should be held in an inclined position, in order that the ammonia may flow less rapidly down the side. A yellow film of silver arsenite will be formed at the surface of contact of the two fluids.

We have in the test-tube three fluid strata: a lower one containing excess of hydrogen nitrate, an upper one containing excess of ammonia, and an intermediate one consisting of a neutral solution of ammonium nitrate. Silver arsenite is insoluble in water, but soluble in excess both of acid and of alkali, and therefore appears only where the fluid is neutral.

On shaking the fluid the yellow film will disappear altogether, unless just enough ammonia has been added to neutralise the acid.

3. With copper sulphate, their solutions, when neutral, give a bright green precipitate.

The details of this test have been given already, p. 368.

Tests for Arsenates.

[The solution of potassium arsenate, already prepared, may be used.]

1. With hydrogen sulphide, they give hardly any precipitate, until reduced to protosalts.

Acidify a portion of the solution of potassium arsenate with hydrogen chloride and divide it into two parts.

(a) Add to one portion some solution of hydrogen sulphide. No precipitate will be produced, and even on heating only a slight yellow precipitate will fall.

(b) Add to the remainder some solution of hydrogen sulphite (or of sodium sulphite mixed with hydrogen sulphate), boil the liquid until it no longer smells of sulphur dioxide, and then test with hydrogen sulphide. A yellow precipitate of

arsenic trisulphide will be formed, the hydrogen arsenate having been reduced to hydrogen arsenite by the action of the hydrogen sulphite.

*2. With silver nitrate, their solutions, when neutral, give a red precipitate.

Acidify another portion with hydrogen nitrate, add a few drops of solution of silver nitrate, and pour on the solution dilute ammonia, as directed, p. 373. A dull-red precipitate of silver arsenate will form at the point where the solution is neutral.

*3. With magnesium sulphate, in presence of ammonium salts, they give a white crystalline precipitate.

Add a few drops of ammonium chloride to another portion, then about the same quantity of ammonium hydrate, and lastly a drop of solution of magnesium sulphate. A white crystalline precipitate will be formed, very similar in appearance, and analogous in composition, to magnesium-ammonium phosphate (p. 301), the phosphorus being replaced by arsenic.

Additional Experiment.

Marsh's test for Arsenic.

This is described on p. 379, *et seq.*, and may be deferred until the reactions of antimony compounds have been examined.

5. ANTIMONY.

[Symbol of atom, Sb (stibium).]

Weight ,, 122 hydrogen-atoms.]

Antimony much resembles arsenic both in its physical properties and in the compounds it forms. It is not, however, so volatile as arsenic, nor does it combine with oxygen quite so readily; but at a bright red heat it becomes vapour and combines with oxygen, if present. Its reduction from its commonest ore, antimony trisulphide, may be illustrated on a small scale as follows.

Mix a little antimony trisulphide with potassium cyanide, and heat the mixture on charcoal before the blowpipe. Brilliant globules of metal will be produced, which lose their lustre at once on being removed from the reducing flame, and white fumes of antimony trioxide are produced and form an incrustation on the cool part of the charcoal. Owing to the volatility of the metal, these white fumes of oxide are emitted for some time after the globule is removed from the flame, especially if a stream of air from the blowpipe is directed upon it. When cold, the globule should be detached from the charcoal, placed in a mortar, and the pestle pressed forcibly down upon it. It will be crushed to powder instead of spreading out into a plate.

Preparation of compounds of Antimony.

[Typical examples,—

Antimony trichloride,

Formula of molecule.

SbCl_3

„ basic chloride,

SbOCl

„ trisulphide,

Sb_2S_3

„ pentoxide,

Sb_2O_5

Ammonium thioantimonite,

$\text{H}_4\text{N SbS}_2$

Potassium-antimonyl tartrate,

$\text{K(SbO)C}_4\text{H}_4\text{O}_6$

1. Antimony trichloride.

The method of preparing this by heating antimony sulphide with hydrogen chloride has been already incidentally mentioned on p. 274. The metal antimony itself is only with difficulty acted on by hydrogen chloride, but readily so by aqua regia.

Place a small fragment (about as large as a pea) of metallic antimony in a strong mortar, and strike it with the pestle. It will, as already observed, split to pieces and may readily be ground into a fine crystalline powder. Put a little of this powder into a test-tube, add 5 or 6 c.c. of strong hydrogen chloride and one or two drops (not more) of hydrogen nitrate, and apply heat. The metal will dissolve pretty readily, forming antimony trichloride. When the action has ceased, allow the liquid to cool, and decant the clear solution into another test-tube for use in experiments.

2. Antimony basic chloride (or oxychloride).

What has been said respecting the basic salts of bismuth p. 363) applies also to antimony: water readily decomposes many of its salts, especially the trichloride, with formation of insoluble compounds in which some of the non-metallic radicals are replaced by oxygen. Antimony tartrate, however, is an exception.

Pour a few drops of the solution of antimony trichloride (prepared just now) into a test-tube and add 5 or 6 c.c. of water. A white precipitate, consisting of antimony oxychloride, will be produced¹. Divide the liquid into two portions:—

(a) To one add a little strong hydrogen chloride. The precipitate will dissolve, and the solution may be reserved for use in expt. 3.

(b) To the other portion add some solution of sodium-hydrogen tartrate. The precipitate will redissolve, sodium-antimonyl tartrate being formed, which is not affected by water.

When potassium-hydrogen tartrate ('cream of tartar') is used instead of the corresponding sodium salt, potassium-antimonyl tartrate is produced, which is the preparation much used in medicine under the name of 'tartar-emetic.'

This reaction serves to distinguish between antimony oxychloride and the corresponding bismuth salt: the latter, as proved already, p. 364, being insoluble in tartrates.

3. Antimony trisulphide.

Take the solution of antimony trichloride containing slight excess of hydrogen chloride, obtained in expt. 2a, and add to it some solution of hydrogen sulphide. An orange precipitate of antimony trisulphide will be formed, which is often used as a paint and also in the manufacture of vulcanised india-rubber.

Observe the difference in colour between this and the native sulphide; the latter being crystalline, while the orange precipitated sulphide is amorphous.

[Keep the contents of the test-tube for a future experiment.]

¹ $\text{SbCl}_3 + \text{H}_2\text{O} = \text{SbOCl} + 2\text{HCl}$

4. Antimony pentoxide.

When strong hydrogen nitrate is poured upon antimony, the metal is not (like most others) dissolved as nitrate, but combines with some of the oxygen of the acid, forming antimony pentoxide.

Put a little powdered antimony into a test-tube, pour over it a few drops of strong hydrogen nitrate, and heat gently. Orange vapours of nitrogen tetroxide will be given off abundantly, and the antimony will be converted into a white powder, the pentoxide, insoluble in the acid.

5. Ammonium thioantimonite (or sulphantimonite).

This is a salt in which antimony forms part of the non-metallic radicle. The thioantimonites are analogous to the thioarsenites (p. 368), and are formed, like the latter, by the action of such sulphides as ammonium sulphide upon antimony trisulphide.

Take the test-tube containing the antimony trisulphide prepared in expt. 3, neutralise the free acid by addition of ammonia (in slight excess if anything), add several drops of ammonium sulphide, and warm the mixture. The precipitate will dissolve, a yellow solution containing ammonium thioantimonite being formed¹.

If to this dilute hydrogen chloride is added in slight excess, the salt will be decomposed and antimony trisulphide precipitated.

These experiments illustrate a method used in analysis for separating antimony (and also arsenic, tin, gold, and platinum) from the other metals of this group, the sulphides of which are not affected by ammonium sulphide.

Potassium hydrate may, as mentioned under ARSENIC, be used instead of ammonium sulphide.

6. Hydrogen antimonide.

This is closely analogous to hydrogen arsenide, and is formed by the action of nascent hydrogen upon compounds of antimony.

¹ $(\text{H}_4\text{N})_2\text{S} + \text{Sb}_2\text{S}_3 = 2\text{H}_4\text{NSbS}_2$

Repeat expt. 5a, p. 369, using a drop of solution of antimony trichloride instead of arsenic trichloride. Hydrogen antimonide will be formed, a gas much resembling hydrogen arsenide in properties, *e.g.* in its offensive smell and its blackening effect on silver nitrate. The distinctions between them will be given under Marsh's test, p. 379.

If expt. 5b is tried, it will be found that *no* hydrogen antimonide is formed on the addition of antimony trichloride to the alkaline solution. This is a point of distinction between antimony and arsenic.

Tests for compounds of Antimony.

*1. Their solutions, especially if they contain hydrogen chloride, give, when mixed with water, a white precipitate, soluble in tartrates.

The details of this test have been given above, p. 376.

*2. Their solutions, acidified with hydrogen chloride, give with hydrogen sulphide an orange precipitate, soluble in ammonium sulphide and potassium hydrate.

The details of this test also have been given already, p. 377.

*3. When placed in contact with zinc and platinum, antimony is reduced on the latter as a black powder.

Place a piece of platinum foil in an evaporating dish; put on it a small fragment of granulated zinc, and pour into the dish a little dilute hydrogen chloride. When the evolution of hydrogen has begun from the surface of the platinum, add a drop or two of the solution of antimony trichloride. The antimony will be thrown down on the platinum as a black coating, owing to galvanic action (p. 79). If the black deposit is heated with a drop of ammonium sulphide it becomes orange¹.

*4. Reduced on charcoal, they give a brittle metallic globule, with a white incrustation.

The mode of performing this test has been described on p. 375.

¹ The platinum may be cleaned from the deposit by warming it with a few drops of strong hydrogen chloride, to which one drop of hydrogen nitrate may be added.

Additional Experiment.

Marsh's Test for Arsenic and Antimony.

Apparatus required.—Small flask; thistle funnel; two elbow-tubes, one with long branch; retort-stand; Bunsen's holder; drying-tube, filled with calcium chloride or quicklime; difficultly-fusible glass tubing, 3 or 4 mm. in internal diameter; Bunsen's burner; Herapath's blowpipe; small porcelain dish, or broken pieces of one; three-square file; test-tubes in basket; small funnel; filters.

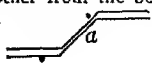
Pure zinc; pure hydrogen sulphate; solutions of silver nitrate, ammonium hydrate, sodium-hydrogen tartrate, hydrogen sulphide; iron sulphide; hydrogen chloride; hydrogen nitrate.

The principle of this test, which is the one commonly used in cases of suspected poisoning by arsenic or antimony compounds, is the formation of hydrogen arsenide or antimonide, and the decomposition of the gas in various characteristic ways. Its delicacy is such that a quantity so small as one-hundredth of a milligramme of arsenic can be detected by it.

A. Detection of Arsenic.

Place a few pieces of granulated zinc in a small flask, fitted with an acid funnel and right-angled elbow-tube, and connect the latter with a drying-tube filled with fragments of calcium chloride or quicklime, and supported in a horizontal position by a Bunsen's holder. Take a piece of difficultly-fusible glass tubing about 4 mm. in internal diameter and 40 cm. in length; soften it in the middle in the flame of a Bunsen's burner¹, and draw the two ends asunder, until the softened portion is contracted to a diameter of 2 mm. When it is cool, make a scratch with a file in the middle of the contracted portion, and break it at that point. You have now two tubes each about 18 cm. in length and terminated by a jet². Reserve one for an experiment with antimony, and connect the other with the drying-tube, supporting it horizontally on the largest ring of the

¹ If the glass is very difficult to fuse, a blowpipe flame may have to be used.

² The jet shown in the figure is turned up. This, which is a slightly preferable form, may be obtained by moving the hands in drawing out the glass, laterally (the one hand towards, the other from the body), so as to give the drawn-out tube the following form . It should then be cut in two at *a*.

retort-stand at such a height that a lamp may be placed underneath it. The whole apparatus will then be arranged thus, fig. 95.

Pour a little water on the zinc in the flask, and add a few drops of strong pure hydrogen sulphate, so as to generate a moderately rapid current of hydrogen. Allow the gas to pass through the apparatus for about two minutes, in order to sweep out all traces of air. While this is going on, you may get ready a right-angled elbow-tube with one long branch, a test-tube half filled with a dilute solution of silver nitrate (five drops of the test-solution to 10 c.c. of water), and one or two pieces of clean glazed porcelain, such as the lid of a crucible, or fragments of an evaporating dish. Now test

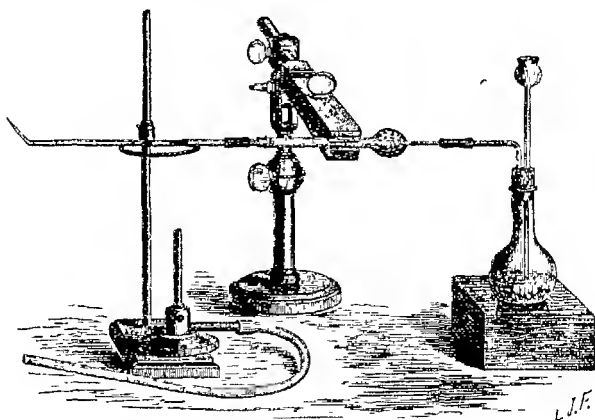


Fig. 95.

the purity of the gas by collecting some in a test-tube held over the jet (see p. 133). When you are quite sure that the gas is unmixed with air, you may light it at the jet and depress into the flame, for a few seconds, one of the pieces of porcelain. If any stain appears on the white surface (as may happen if the zinc or hydrogen sulphate is contaminated with arsenic) allow the stream of gas to pass a little longer, and do not proceed with the experiment until the porcelain depressed on the flame remains unstained.

[If after several trials the stain still appears, the zinc, or the acid, or both, are impure, and other samples must be used.]

When this is the case, pour into the funnel about two drops (not more) of a solution of arsenic chloride, and wash it down into the flask with a little water. The first effect of this will be to increase

the evolution of gas, and the flame of the jet will shortly become tinged with gray (not unlike the colour imparted to flame by the presence of potassium vapour). Hydrogen arsenide is now being formed, and you may proceed to decompose it in the three following ways:—

(a) By the heat produced by its own combustion.

Place in the flame a clean cold surface of glazed porcelain, depressing it until it almost touches the jet from which the gas is issuing. A black spot, consisting of metallic arsenic or of a lower hydride, will be formed on the white surface. Two or three of these should be made on different pieces of porcelain, and reserved for future examination¹.

(b) By heat applied to the tube through which the gas is passing.

Place a lamp with a small flame underneath the tube near the end at which the gas enters, and heat that part of the tube to redness. A black shining ring of arsenic will be deposited just beyond the heated portion of the tube, while the flame at the jet will lose its gray colour, showing that the arsenic has been arrested in its course to the jet.

(c) By a solution of silver nitrate.

Detach the drying-tube (and the tube containing the arsenic deposit), and fit in its place the elbow-tube, the longer branch of which should reach to the bottom of the test-tube containing the solution of silver nitrate: the latter may be supported in an upright position by the smallest ring of the retort-stand. Pour, if necessary, a little more acid and solution of arsenic chloride into the flask. The solution of silver nitrate will soon become turbid, and a black deposit of metallic silver will be formed, while silver arsenite will remain in solution in the hydrogen nitrate which is formed².

[The evolution of gas should now be stopped, by taking the cork out of the flask and pouring the solution away from the zinc, which latter, after being thoroughly washed, may be retained in the flask for a similar experiment with antimony; which should be made now, if time permits, so that the results may be compared with those obtained from arsenic.]

¹ They are formed for the same reason that soot is deposited on a plate held in a candle-flame. The hydrogen arsenide is decomposed by the heat of combustion: the hydrogen combines with oxygen to form water, while only a portion of the arsenic can obtain enough oxygen to form the trioxide; the rest is suspended in the flame and deposited on any cold surface brought into contact with it.

² $\text{H}_3\text{As} + 9\text{AgNO}_3 + 3\text{H}_2\text{O} = \text{Ag}_7\text{AsO}_3 + 9\text{HNO}_3 + 3\text{Ag}$

You have now three results of the decomposition of the hydrogen arsenide, which are to be further examined.

(a) **The spots on the porcelain.**

Dip a glass rod in strong hydrogen nitrate, and moisten one of the spots with it. The metal will dissolve in the acid, especially if the porcelain be gently warmed, and on evaporation a white residue of hydrogen arsenate will be left. Add another drop of acid, and again evaporate to dryness, to ensure the complete oxidation of the arsenic. Do not raise the temperature beyond the point necessary to drive off the excess of hydrogen nitrate, lest the hydrogen arsenate should be itself decomposed. Moisten the residue with a drop of solution of silver nitrate and again evaporate to dryness. A red deposit of silver arsenate will be left, readily seen on the white porcelain.

(b) **The deposit formed in the tube.**

Connect the tube with a drying-tube (filled with calcium chloride, not quicklime), and arrange them as before, when the deposit was to be formed (placing the whole in a draught-cupboard, if possible). In place of the hydrogen generating flask attach to the drying-tube, a test-tube fitted with a thistle funnel and elbow-tube, and containing one or two lumps of iron sulphide and a little water. Pour down the funnel a few drops of strong hydrogen chloride, just sufficient to liberate a slow stream of hydrogen sulphide gas. When the air has been expelled from the apparatus, light the gas at the jet (merely to prevent its escape into the room), and heat the metallic deposit by a lamp with a very small flame, beginning at its outer border, or that farthest from the end at which the gas enters. The arsenic as it volatilises will decompose the hydrogen sulphide, combining with its sulphur and forming a yellow ring of arsenic trisulphide in the cool part of the tube, which is very volatile and may be driven about from one part of the tube to another by the heat of the lamp.

(c) **The solution containing silver arsenite.**

Filter this from the reduced silver, and pour gently upon its surface some very dilute solution of ammonia from a pipette (see expt. 2, p. 372). A yellow statum of silver arsenite will be formed at the point where the solution is neutral.

B. Detection of Antimony.

Hydrogen antimonide can be decomposed in the same ways as hydrogen arsenide, but with results which enable us to distinguish it without difficulty from the latter.

Arrange an apparatus similar to that already described in the case of arsenic. After making sure that the hydrogen evolved is pure and leaves no stain upon the porcelain, pour into the funnel two drops of solution of antimony trichloride, and wash it down with a little dilute hydrogen sulphate. Then proceed with the experiments precisely as already directed for arsenic, and compare the results obtained in the two cases.

(a) Decomposition of the gas by the heat of combustion.

The dark spots formed on the porcelain are more like soot, and not so brown and lustrous as those of arsenic. They leave a white residue when treated with hydrogen nitrate, but yield no red deposit with silver nitrate¹.

(b) Formation of a black deposit of antimony in the heated tube, and subsequent conversion of this into sulphide, by passing hydrogen sulphide over it.

A dark orange-red film of antimony trisulphide will be formed, close to the deposit in the tube, which is only volatilized with difficulty, by the utmost heat of the lamp.

(c) Decomposition of the gas when passed into solution of silver nitrate.

The whole of the antimony is precipitated as silver antimonide². No yellow layer or precipitate, therefore, is seen when the filtrate is neutralised by ammonia. In order to prove the presence of antimony in the precipitate, wash it on the filter, then place the portion of the filter which contains the precipitate in a beaker and boil it with a little solution of sodium-hydrogen tartrate together with one or two drops of hydrogen chloride, when the antimony will dissolve while the silver will remain as insoluble chloride. Filter the solution and test it with hydrogen sulphide, which will give the characteristic orange precipitate of antimony trisulphide.

It is obvious that in cases where we have both antimony and arsenic in the same solution this last test gives us a means of separating the two metals, the antimony being found in the precipitate produced when the gases are passed into the silver nitrate solution, while the arsenic remains in solution.

The two metals may also be discriminated by the difference in volatility of their sulphides. When the mixed metallic deposit

¹ A black deposit of reduced silver is sometimes formed, if a sufficient excess of hydrogen nitrate has not been added.

² $\text{H}_3\text{Sb} + 3\text{AgNO}_3 = 3\text{HNO}_3 + \text{Ag}_3\text{Sb}$

in the tube is heated in a current of hydrogen sulphide, the yellow ring of arsenic trisulphide is always deposited considerably in advance of the orange sublimate of antimony trisulphide.

6. TIN.

[Symbol of atom, Sn (stannum).]

Weight „ 118 hydrogen-atoms.]

The chief ore of tin is the dioxide ('tin-stone'), and an experiment has already been made, p. 102, showing how oxygen can be taken away from tin dioxide by heating it on charcoal with some flux. The ore is thus reduced on a large scale, coal or coke being employed, with fluor spar as a flux.

Crystalline character of Tin.

Cast tin, although to a certain extent tough and malleable, so that it can be rolled out into sheets only $\frac{1}{16}$ mm. in thickness (the ordinary tinfoil) is yet decidedly crystalline in structure; as may be proved in several ways.

(a) Take a strip of tin (the best tin is usually sold in strips or thin rods), bend it quickly backwards and forwards several times, holding it to the ear while doing so. A crackling sound will be heard, and the metal will become sensibly warm at the point of flexure. This is due to the motion of the crystals over each other, and their mutual friction.

(b) Wash the surface of a strip of tin plate¹ (which is sheet iron coated with tin) with a little alcohol to free it from grease, and then, after rinsing it with water, apply with a piece of sponge or tow a mixture of 5 c.c. dilute hydrogen chloride with 2 c.c. of dilute hydrogen nitrate (the ordinary laboratory solutions). The bright surface will soon show a variety of irregular patches, somewhat like 'watered' silk, and should then be well washed with clean water, to stop further action of the acid. The reason is, that the film of tin upon the iron consists of numerous small

¹ A piece of pure tinfoil shows the effect even more strikingly, and may be used, if at hand.

crystals buried in a mass of less crystalline material. The acid attacks the latter more readily than the crystals, and lays bare the faces of the latter, showing their symmetrical arrangement, like masses of soldiers all facing the same way.

Alloys of Tin.

Two of these—its amalgam with mercury (p. 331) and ‘fusible metal’ (p. 362)—have been prepared already. Tin also unites with iron at a temperature only slightly above its melting-point (230°), and this property is of importance in the manufacture of tin plate, since it causes the coating of tin to adhere firmly to the sheet of iron. The mode in which tin plate is manufactured may be illustrated as follows.

Clean a strip of sheet iron, first with emery paper, and then by placing it for half a minute in a little dilute hydrogen sulphate in a plate. Melt a few grammes of tin in an iron dish, or small ladle. As soon as it is all melted, sprinkle a little powdered ammonium chloride (as a flux) on its surface, and when this begins to volatilise dip the end of the cleaned strip of iron into the metal, and stir it about. The tin will soon begin to unite superficially with the iron, covering it with a uniform bright film.

The process of soldering, by which iron, copper, brass, &c., are joined together, depends upon the similar formation of superficial alloys at the parts to be joined; and the ‘soft solder’ used by tin-smiths is an alloy of tin and lead.

Preparation of compounds of Tin.

	Formula of molecule.
[Typical examples,—Tin protochloride,	SnCl_2
„ perchloride,	SnCl_4
„ dioxide,	SnO_2]

Tin, like mercury, forms two well-defined series of salts, in one of which it is divalent, in the other tetravalent. The conditions necessary for the formation of each series are, presence of excess of the metal for the protosalts, and of excess of the acid radicle for the persalts.

1. Tin protochloride (stannous chloride).

Place about 2 grms. of *pure* tin-foil¹ in a large test-tube, add 10 c.c. of strong hydrogen chloride, and boil for a quarter of an hour. Hydrogen will be evolved, the metal taking its place and forming tin protochloride². Pour off the solution while a little of the metal still remains undissolved, dilute it with water to 30 c.c., and reserve it in a corked tube or bottle for experiments, placing in it a small bit of metallic tin to prevent its passing into the state of persalt.

2. Tin perchloride (stannic chloride).

Put 1 grm. of tin-foil into a test-tube, pour on it 5 c.c. of strong hydrogen chloride, and two drops (not more³) of strong hydrogen nitrate, and heat gently. The metal will readily combine with the chlorine evolved from the aqua regia to form tin perchloride; and when the solution is complete the liquid should be poured into a porcelain dish and evaporated on the sandbath, about 1 c.c. of strong hydrogen nitrate being added to convert any remaining protosalt into persalt (which it does, of course, by causing the liberation of chlorine, p. 239). To make sure that the conversion into perchloride is complete, take out a drop or two of the liquid with a pipette, dilute it with water, and test it with a drop of mercury perchloride. If any precipitate is produced, some tin protochloride still remains, and a few more drops of hydrogen nitrate must be added. Finally, evaporate the solution to half its original bulk (stopping the evaporation when white fumes of the perchloride appear), dilute it with water to 30 c.c., and reserve the solution for experiments.

3. Tin dioxide, and Stannates.

Tin dioxide is always formed when tin is heated above its melting-point in air, as has been done already, p. 103. It can be made to combine with water to form an acid, hydrogen stannate (H_2SnO_3), from which other stannates are obtainable: thus

¹ See p. 22, note. If tin-foil is not at hand, a little tin should be granulated as directed in the case of zinc (p. 25).

² $2HCl + Sn = SnCl_2 + H_2$

³ If much hydrogen nitrate is added at once, the tin may be precipitated as perhydrate.

tin shows a certain analogy to arsenic and antimony in being capable of forming part of a non-metallic radicle. This acid is formed when potassium hydrate is added to a solution of a tin persalt.

(a) Put a few drops of the solution of tin perchloride into a test-tube, dilute with water and add solution of potassium hydrate, drop by drop, shaking the mixture after each addition. When the free acid in the solution has been neutralised, a permanent precipitate will be formed, which is hydrogen stannate. On adding excess of the potassium hydrate, the precipitate will be redissolved, potassium stannate (K_2SnO_3)¹ being formed.

This salt (and also the perchloride) is extensively used in dyeing, from its action on colouring matters as a 'mordant'; a term which will be explained and illustrated under ALUMINIUM.

(b) Another similar acid, hydrogen metastannate ($H_{10}Sn_5O_{15}$), is formed by the action of strong hydrogen nitrate on metallic tin (compare its action on antimony, p. 377).

Place a bit of tin foil (or granulated tin) in a test-tube, and pour on it some strong hydrogen nitrate. Notice the violent action, the evolution of orange vapours of nitrogen tetroxide, and the formation of a white powder, hydrogen metastannate, which is insoluble in excess of the acid.

Properties of compounds of Tin.

A. Protosalts (Stannous Salts).

[The solution of tin protochloride already made, may be used.]

*1. Their solutions, when tested with hydrogen sulphide, give a dark brown precipitate, soluble in potassium hydrate and ammonium sulphide.

Add excess of solution of hydrogen sulphide to a portion of the solution of tin protochloride. A dark brown, nearly

¹ Notice the analogy of this formula to those of the carbonates and silicates.

black precipitate of tin protosulphide will be formed. Divide the mixture into two portions:—

(a) To one add some solution of potassium hydrate (which must be fairly pure and free from carbonate), and warm it. The precipitate will redissolve, a double sulphide of tin and potassium being formed. On addition of dilute hydrogen chloride to this, the brown protosulphide will be reprecipitated.

(b) To the other portion add a slight excess of ammonia, then some solution of ammonium sulphide (which should be yellow, showing the presence of higher sulphides), and warm the mixture. The precipitate will redissolve, as in the last experiment, but in this case a higher sulphide of tin is formed (a process analogous to oxidation), *viz.* tin disulphide, which forms a salt called ammonium thioannate¹. On addition of excess of dilute hydrogen chloride to the clear solution, a light yellow precipitate of tin disulphide will be formed.

***2. With mercury perchloride they give a white precipitate, quickly turning gray.**

To another portion add a drop of solution of mercury perchloride. A white precipitate of mercury protochloride will be produced, the colour of which changes, however, immediately to gray (the tin salt being in excess) owing to its reduction to metallic mercury².

The protosalts of tin are, in fact, very powerful and useful reducing agents, as has been illustrated in the case of mercury salts, p. 340.

***3. Reduced in contact with zinc and platinum they yield a gray spongy deposit of metal.**

Put a piece of platinum-foil in a porcelain dish, add a little dilute hydrogen chloride, and drop in a bit of granulated zinc. Hydrogen will, of course, be evolved. Now add one or two drops of solution of tin protochloride; metallic tin will be quickly reduced as a porous, moss-like mass (similar to the 'lead-tree,' p. 349) chiefly round the zinc, and readily washed

¹ $(\text{H}_4\text{N})_2\text{S} + \text{SnS}_2 = (\text{H}_4\text{N})_2\text{SnS}_3$

² (i) $\text{SnCl}_2 + 2 \text{HgCl}_2 = \text{SnCl}_4 + \text{Hg}_2\text{Cl}_2$

(ii) $\text{SnCl}_2 + \text{Hg}_2\text{Cl}_2 = \text{SnCl}_4 + 2 \text{Hg}$

away from both the zinc and the platinum by a stream of water. Compare the similar experiment with antimony, p. 378, in which the deposit obtained was formed on the platinum alone, black, and closely adherent.

***4. Reduced on charcoal, they yield a malleable metallic globule, with a white incrustation.**

The mode of performing this experiment has been already given, p. 103.

B. Persalts (Stannic Salts).

[The solution of tin perchloride (p. 386) may be used.]

***1. Their solutions, when tested with hydrogen sulphide, give a yellow precipitate, soluble in potassium hydrate and ammonium sulphide.**

Add solution of hydrogen sulphide to a portion of the solution of tin perchloride, and apply heat. A light yellow precipitate of tin disulphide will be formed, increased in quantity and rendered flocculent, as the temperature rises. Divide the liquid into two portions and try its solubility in potassium hydrate and ammonium sulphide as directed in the case of the protosalts, p. 388.

***2. With mercuric perchloride they give no precipitate.**

An atom of tin, in fact, cannot hold more than four atoms of chlorine in combination; and in the persalts it is already combined with this quantity, and so cannot take chlorine from other substances.

***3. Reduced in contact with zinc and platinum. }**

***4. Reduced on charcoal before the blowpipe. }**

The results with these two tests are the same as in the case of the protosalts.

•

7. GOLD.

[Symbol of atom, Au (aurum).]

Weight „ 197 hydrogen-atoms.]

[Solutions containing gold should not, of course, be thrown away, but put into a bottle labelled 'Gold Residues.' For the method of recovering gold from them, see Appendix B. II.]

Preparation of Gold trichloride.

, [Formula of molecule, Au Cl_3 .]

Gold is a metal which is acted on by very few things, even the strongest acids and caustic alkalies failing to attack it. But nascent chlorine combines with it readily, and this is most usually obtained by mixing hydrogen chloride with hydrogen nitrate (p. 239): the name 'aqua regia,' applied to this mixture, being derived from the fact that it dissolves gold, the 'rex' or king of metals.

Place a leaf of gold in a dry, warm test-tube, by placing the slightly damp end of a glass rod in contact with one edge of the leaf, rolling the latter round the rod, then transferring it to the tube and unrolling it within. Add about 2 c.c. of strong hydrogen chloride, and observe that the metal will not dissolve in the acid, even on boiling. Treat another leaf of gold with hydrogen nitrate in a similar way; it also will be found to be unacted upon. Now mix the contents of the two tubes; the metal will at once combine with the chlorine in the 'aqua regia' thus formed, and a yellow solution of gold perchloride will be obtained. Pour this into a porcelain dish, add two or three more leaves of gold and a little more hydrogen chloride, and evaporate the solution on a sandbath nearly, but not quite, to dryness; since if the residue is heated much above 100° , an insoluble protochloride (Au Cl) may be formed.

[In cases where an evaporation has to be carried on, or a substance heated, at a temperature not exceeding 100° , the heat is best applied by boiling water. A simple water-bath consists of a beaker one-third filled with water kept boiling over a lamp; on it is placed the dish containing the substance, resting on three bits of copper wire or sheet lead bent over the top edge of the beaker, so as to leave a small interval through which the steam escapes.]

Dilute the liquid with about 15 c.c. of water and use it in the following experiments.

There are no other compounds of gold of sufficient importance to be worth preparing: one or two of them will be mentioned in the description of the tests for the metal.

Tests for compounds of Gold.

1. Their solutions, acidified and tested with hydrogen sulphide, give a black precipitate, soluble in potassium hydrate and ammonium sulphide.

Add excess of hydrogen sulphide to a portion of the solution of gold trichloride, and warm the mixture. A black precipitate (or if the solution is dilute, a deep black liquid) will be obtained, which will slowly dissolve on addition of excess of potassium hydrate, forming a nearly colourless solution of potassium thioaurate.

*2. With iron protosulphate they yield a brown precipitate of metallic gold.

Add to another portion some solution of iron protosulphate. The liquid will rapidly darken, and metallic gold will be precipitated as a brownish powder (the liquid in which the precipitate is suspended having a blue or green colour by transmitted light), or if the solution is strong, as a spongy mass. If the quantity of precipitate is sufficient, it may be washed by decantation and dried in a watch-glass; if a portion of it be then burnished with the end of a glass rod or of a test-tube, it will acquire the metallic yellow lustre of gold.

*3. With tin chloride they yield a purple precipitate ('Purple of Cassius').

Test another portion of the solution of gold trichloride with solution of tin protochloride to which one drop of iron perchloride has been added (in order to form a little tin perchloride in the liquid). A brownish purple precipitate will be formed, called from its discoverer, the 'purple of Cassius,' containing gold, tin, and oxygen, but not, apparently, of definite composition. This substance is extensively used in gilding porcelain and china, and imparting a purple-red colour to glass. When the solutions are very dilute, the colour of the liquid changes to brownish red, but no precipitate falls which can be separated by filtration.

Additional Experiment.

Transparency of Gold leaf.

Gold is the only metal which has with certainty been reduced to sheets so thin that light will pass through them; their thickness being, in fact, no greater than $\frac{1}{100000}$ mm.

In order to examine this, it is best to spread out the leaf flat upon a glass plate, which may be done in the following way.

Clean the glass plate, which should be about 15 cm. square, with a tuft of cotton-wool dipped in alcohol, dry it with a clean cloth, warm it (to insure perfect dryness), and lay it flat on the table. Slightly damp the edge of a paper-knife or a glass rod, and lay it on one edge of the leaf of gold, to which it will adhere; you can then transfer the leaf to the plate and lay it approximately flat on the glass. Detach the paper-knife from the gold by slightly rubbing it against the glass, and then, still keeping the glass horizontal, direct a very gentle stream of water from a wash-bottle under the leaf of gold. The water will spread quickly over the glass, and the leaf will float on it, losing all inequalities and wrinkles. Now raise very carefully and slowly one corner of the glass, holding a glass rod at the opposite corner to guide the water in flowing off, and absorb the remaining water with blotting-paper; finally gently warm the plate over a lamp until it is perfectly dry. The leaf of gold is left as a perfectly smooth film on the glass. Hold it up to the light, and notice the deep green colour of the transmitted light. Examine it with a magnifier; many holes will be seen, and much inequality of thickness, but the greater portion of the leaf is a continuous film, even under high magnifying powers.

8. PLATINUM.

[Symbol of atom, Pt.

Weight „ 197 hydrogen-atoms.]

[All waste solutions, &c., containing platinum should be put into a bottle labelled 'Platinum Residues.' To recover the metal from them they may be treated as directed in Appendix B. II.]

Platinum, from its infusibility (in all ordinary flames), its malleability and ductility (as shown by the thin foil and wire made of it), and its unalterability by most substances (even strong acids), is most valuable in chemical work. It should be

borne in mind, however, that it readily forms fusible alloys with some metals, *e.g.* copper and lead (as may have been noticed in blowpipe work), and also that caustic alkalis, nitrates, and chlorine act easily upon it: so that nothing should be heated on platinum without considering whether the substance is likely to injure the foil or wire used as the support.

Preparation* of compounds of Platinum.

	Formula of molecule.
[Typical examples,—Platinum perchloride,	Pt Cl_4
Platinum-ammonium chloride, $\text{Pt}(\text{H}_4\text{N})\text{Cl}_5$]	

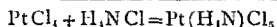
1. Platinum perchloride.

For the experiments on platinum compounds the ordinary laboratory solution of platinum perchloride may be used; but if you have any waste scraps of platinum foil or wire they may be converted into the tetrachloride in the following way.

Measure 6 c.c. of strong hydrogen chloride into a large test-tube, add 2 c.c. of strong hydrogen nitrate, drop in about 0.2 gm. of thin platinum foil or wire, and heat the tube on the sandbath. Platinum, like gold, is not soluble either in hydrogen chloride or in hydrogen nitrate, but is readily acted upon by the chlorine evolved during the mutual decomposition of these acids, and dissolves as perchloride. Evaporate the solution in a dish, in a draught-cupboard or the open air, observing the same precautions as in the case of gold, since an insoluble platinum protochloride (PtCl_2) is formed if the temperature is high. Dilute the solution with about 10 c.c. of water for use in the following experiments.

2. Platinum-ammonium chloride.

Put about 3 c.c. of a solution of platinum perchloride into a test-tube, add an equal volume of *saturated* solution of ammonium chloride, and shake the mixture. A yellow, crystalline precipitate of platinum-ammonium chloride will be formed¹,



¹ The ordinary platinum-foil, &c. often contains iridium. If this is the case, the solution of the perchloride will be deep red, and the precipitate formed by ammonium chloride will be dull buck-red, instead of yellow. The presence of iridium will not, however, interfere with the experiments.

the separation of which will be hastened by the addition of 5 or 6 c.c. of common alcohol (in which the salt is less soluble than in water). Leave the precipitate to subside for a few minutes; then pour the whole on a small filter, and wash it with water to which about one-fourth its volume of alcohol has been added, rinsing the precipitate as much as possible down to the point of the filter. Lastly, dry it on the filter at a gentle heat, while other experiments are proceeded with.

3. Spongy platinum.

This is the condition in which the metal is obtained by gently igniting platinum-ammonium chloride.

Take the dry (or partially dry) filter containing the precipitate of platinum-ammonium chloride, cut off the part of it which contains the precipitate, fold this up as closely as possible, and coil the end of a piece of platinum wire two or three times round it, so as to form a compact bundle. Heat this gradually to low redness over the flame of a Bunsen's burner, until all the paper has been burnt away and nothing remains but a gray mass of metallic platinum. During the ignition ammonia and chlorine are given off, and the skeleton of metal which remains is highly porous and has the property of absorbing large quantities of gases. It should be kept for use in the following experiments.

[Platinum may be obtained in a state of division still finer than platinum sponge—in particles so fine, in fact, that they almost cease to reflect light, and form a black impalpable powder. The readiest method of preparing 'platinum black' is to add excess of sodium carbonate to platinum perchloride, and then to boil the liquid with a little grape sugar. Carbon dioxide is evolved with strong effervescence, and a black powder is formed (gradually, if the solution is dilute), which should be washed by decantation successively with dilute alcohol, hydrogen chloride, potassium hydrate, and finally water, and then dried at a gentle heat. This powder is still more effective than spongy platinum in producing chemical combination.]

Action of Platinum in causing chemical combination.

This is best shown when the metal is in a finely-divided

state, as in the form of spongy platinum and platinum black. But even platinum in the ordinary compact condition shows the same property to a certain extent, as has been already illustrated in the oxidation of ammonia, p. 154. The action is thought to be due to the power possessed by platinum of condensing gases upon its surface, and thus bringing the molecules closely into contact.

1. Combination of oxygen with hydrogen.

[This may have been tried already, in the course of experiments with hydrogen (p. 134): if so, experiment (a) may be omitted.]

(a) Fit a glass jet by means of a cork to a moderate-sized test-tube; put into the latter a bit of granulated zinc and pour on it some dilute hydrogen sulphate; then fit the cork again into its place. Allow the stream of hydrogen to escape for at least a minute, and test its purity by collecting some in a test-tube, as directed on p. 133. When pure hydrogen is issuing from the jet, hold a little in front of it the spongy platinum already prepared, still held in the coil of wire. It will become red-hot, owing to the combination at its surface of the hydrogen with the oxygen of the air, and the gas will ignite at the jet¹.

(b) Hold the spongy platinum in a stream of coal gas and air (not ignited) issuing from the tube of a Bunsen's burner. The metal will become red-hot, but the gas will not ignite, since coal gas requires a higher temperature than hydrogen to kindle it.

(c) Place a piece of fine wire gauze on the chimney of an alcohol burner, and put upright upon it a cylinder of platinum-foil, made by rolling it loosely round a small test-tube. Turn on the gas partially, and light it above the wire gauze. When the platinum has become red-hot, extinguish the flame by pinching the india-rubber connecting tube, and immediately (before the platinum has had time to cool entirely) allow the gas to flow again. The platinum will begin to glow afresh, and maintain a steady red heat. If a dry gas bottle is held close over it, moisture will be deposited, and the presence of carbon dioxide may be proved in the usual way.

¹ If the spongy platinum has been exposed to the air for some time, it may be necessary to ignite it gently afresh, and let it cool before use.

2. Combination of ether with oxygen.

Pour a few drops of ether into a beaker or wine-glass, and cover the glass partially with a card, to the centre of which is attached the wire carrying the spongy platinum (or a coil of platinum wire) previously heated to redness in a lamp, so that it may hang down within the glass nearly to the bottom. Pungent vapours of aldehyd are at once produced, and this compound is further oxidised to hydrogen acetate. The presence of the latter may be shown by holding in the beaker a strip of blue litmus paper, which will be strongly reddened¹.

Tests for compounds of Platinum.

[The solution of platinum perchloride may be used.]

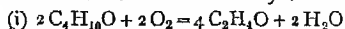
*1. Their solutions, when acidified and tested with hydrogen sulphide, give a black precipitate, soluble in potassium hydrate and ammonium sulphide.

Dilute a few drops of the solution with 5 or 6 c.c. of water, add solution of hydrogen sulphide, and warm it. A black precipitate of platinum persulphide will be formed, which will dissolve, but only with difficulty, in excess of solution of potassium hydrate.

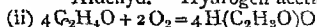
*2. With potassium salts they give a yellow crystalline precipitate.

Add a few drops of dilute hydrogen chloride to a little of the solution of platinum perchloride (which should not be diluted with water), and then a drop or two (not sufficient to neutralise the acid) of solution of potassium hydrate, and stir the mixture with a glass rod if the precipitate does not form at once. A yellow crystalline precipitate will be more or less quickly formed, especially along the lines where the sides of the tube were touched by the glass rod. This consists of platinum-potassium chloride (KPtCl_6), analogous to the platinum-ammonium chloride already prepared.

¹ The successive stages of the oxidation may be expressed as follows:—
Ether. Aldehyd.



Aldehyd. Hydrogen acetate.



Group III.

Metals which are separated from solutions by

Ammonium sulphide.

IRON, COBALT, NICKEL, MANGANESE, CHROMIUM, ALUMINIUM,
ZINC.

1. IRON.

[Symbol of atom, Fe (ferrum).]

Weight „ 56 hydrogen-atoms.]

The most valuable ores of iron are the oxides, occurring in the minerals Haematite (Fe_2O_3) and Magnetite (Fe_3O_4), and the carbonate, Clay Ironstone (Fe CO_3). For the process of smelting these ores a text-book must be referred to; the action of the reducing gases obtained from coal upon iron oxides may be shown on a small scale as follows:—

Powder a little haematite (or rouge, if haematite is not at hand) very finely, and put some into the bend of a roasting-tube, fig. 91, p. 343. Connect the long branch of the tube with the gas supply, pass a moderate stream of coal gas through it (the rapidity of the current can be judged of by lighting the gas at the outer end of the tube), and heat the iron oxide in the flame of a Bunsen burner. The red substance will soon turn black owing to its reduction to metallic iron; oxygen having been withdrawn from it by the carbon monoxide (which plays the most important part in the actual smelting furnace), hydrogen, &c., present in coal gas. Allow the reduced metal to cool, still continuing a slow stream of gas, to prevent access of oxygen; and use it in expt. 2 (b).

Preparation of compounds of Iron.

	Formula of molecule
[Typical examples,—Iron magnetic oxide,	Fe_3O_4
„ peroxide,	Fe_2O_3
„ protosulphate,	FeSO_4
„ persulphate,	$\text{Fe}_2(\text{SO}_4)_3$]

1. Iron magnetic oxide.

Clean a small strip of sheet iron with a file or with emery

paper, until it shows a bright metallic surface; then hold it with a pair of pliers or crucible tongs in the flame of a Bunsen's burner or spirit lamp. The surface will soon lose its lustre, becoming in succession light yellow, orange, blue, and finally dark gray, owing to the formation of an extremely thin film of oxide. If the strip of iron be maintained at a red heat for a few minutes (in a Herapath blowpipe flame or in an ordinary fire), the film of oxide will increase in thickness, and will be detached in the form of black scales when the iron is quenched in a beaker of cold water. These scales consist of the same iron oxide as that which was formed when the watch-spring was burnt in oxygen (p. 123). When the black particles have settled to the bottom of the beaker, hold a magnet just under them, close to the glass, and observe that they are attracted by it, ranging themselves in lines as it is passed underneath them. From this property, and from its identity in composition with the native lodestone, this oxide of iron is called the magnetic oxide.

2. Iron peroxide (ferric oxide)¹.

(a) Fill the bulb of an ignition-tube with powdered iron protosulphate, and heat it strongly in the flame of a Bunsen's burner, holding it nearly horizontally in the crucible tongs. The salt will first melt in its water of crystallisation, then it will turn white, give off water vapour, and lastly, as the temperature rises nearly to redness, it will be decomposed, giving off vapours of sulphur dioxide and trioxide, the latter of which will combine with the water to form an extremely strong kind of hydrogen sulphate, which will redden litmus-paper held at the mouth of the tube. A red residue will remain in the bulb, which consists of iron peroxide, or sesquioxide² (the ordinary 'rouge' used for polishing, &c.).

[This illustrates the derivation of the term 'oil of vitriol' applied

¹ This (as well as the corresponding oxides of the other metals of this group) is often called a 'sesquioxide' (Lat. *sesqui*, one and a half); since the weights of iron and oxygen present in the molecule are in the proportion of the weight of one iron-atom to one and a half times the weight of the oxygen-atom.

² $4\text{FeSO}_4 + \text{H}_2\text{O} = 2\text{Fe}_2\text{O}_3 + 2\text{SO}_2 + \text{H}_2\text{S}_2\text{O}_7$

to hydrogen sulphate, since the old name for iron protosulphate is 'green vitriol.' The acid thus obtained is called 'Nordhausen acid' from the place where it is made.]

(b) Take the tube containing the reduced iron made just now, p. 397, heat the black powder slightly if it has become quite cold, and shake it out upon a plate. It will catch fire as it falls through the air, combining with oxygen and forming iron peroxide.

[This 'pyrophoric' property of finely divided iron is more decided when rouge has been taken for reduction. If no ignition is observed, put the powder into an iron capsule and heat it slightly in the air.]

3. Iron protosulphide.

The preparation of this has been described already, p. 270.

4. Iron proto- and per-sulphates.

Iron forms at least two well-defined series of salts, in one of which (the protosalts) 1 atom of the metal replaces 2 atoms of a monovalent radicle, such as hydrogen; in the other (the persalts) 1 atom replaces 3 atoms (or 2 atoms replace 6 atoms) of a similar radicle¹.

The conditions necessary to form them are, as usual, excess of the metal for the protosalts, and excess of the non-metallic radicle for the persalts. But the oxygen of the air, or that dissolved in the water, so readily determines the change of valency that it must be excluded as far as possible in preparing the protosalts.

A. Iron protosulphate (ferrous sulphate).

Take about 2 gms. of fine iron wire (or of iron filings, if wire is not at hand), clean it from rust, if necessary, by drawing it between folds of emery-paper, form it into a small close coil and place it in a moderate-sized test-tube, in which must be inserted a cork fitted with a glass jet to allow gas to escape. Pour on the iron about 10 or 12 c.c. of dilute hydrogen sulphate,

¹ This will be seen by comparing the formulae of each of the two iron sulphates with that of a quantity of hydrogen sulphate containing the same number of atoms of the sulphate radicle.

Iron protosulphate, FeSO_4	}	Iron persulphate, $\text{Fe}_2(\text{SO}_4)_3$
Hydrogen sulphate, H_2SO_4		Hydrogen sulphate, $\text{H}_2(\text{SO}_4)_3$

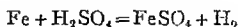
add a few drops of the strong acid, and warm gently if the action appears slow. Hydrogen gas will be given off with effervescence¹, the iron taking its place and forming iron protosulphate (compare the action of zinc on hydrogen sulphate, p. 125). Allow the action to go on for 10 or 12 minutes (keeping up a brisk action by warming the liquid and adding a little more strong acid when required) while other experiments, such as those on p. 405, are proceeded with. When nearly (but not quite) all the iron has dissolved, pour half the solution into a small porcelain dish, and reserve the rest (taking especial care that some metallic iron remains in it undissolved, and that the tube is kept corked, otherwise some persalt will be formed) for experiments on the protosalts.

B. Iron persulphate (ferric sulphate). *

To prepare this from the protosulphate we have, practically, to cause two molecules of the salt $[2 \text{FeSO}_4]$ to take up one atom of the sulphate radicle $[\text{SO}_4]$ and form a molecule of the persulphate $[\text{Fe}_2(\text{SO}_4)_3]$. Excess of acid must therefore be present, and also some oxidising agent, such as hydrogen nitrate, the oxygen from which may combine with the hydrogen of a molecule of the acid, and leave the sulphate radicle free to unite with the iron protosulphate.

Take the portion of the solution which was poured off just now into the dish, add a few drops of dilute hydrogen sulphate, and heat it gently on a sandbath. Add strong hydrogen nitrate, a drop at a time, as long as the addition of a drop causes a transient brown colour in the liquid². Leave the dish exposed to a gentle heat for some minutes (in order to drive off any excess of hydrogen nitrate) while the following experiments are tried.

1



Observe the strong peculiar smell of the gas (pure hydrogen having no perceptible smell), which is due to the presence of traces of compounds of hydrogen and carbon, the latter element being always present in ordinary iron.

² The reason of this will be evident from the experiment already made with nitrates (p. 164). The hydrogen nitrate, by the loss of oxygen, is reduced to nitrogen dioxide, which unites with the iron salt, forming a brown compound easily decomposed by heat.

Properties of Iron protosalts (Ferrous salts).

[These are so very readily converted into persalts by mere exposure for a few moments to air or to water containing air, that it is rather difficult to observe their true reactions. In the following experiments a drop or two of the solution of iron protosulphate should be added to the tube already containing the test solution, and the cork must be replaced at once.]

1. Their solutions, when acidified and tested with hydrogen sulphide, give no precipitate or change of colour.

Pour into a test-tube 2 or 3 c.c. of solution of hydrogen sulphide, and about two drops of the solution of iron protosulphate (which should be strongly acid to test-paper). This will produce no change, showing that iron differs from the group of metals last considered in not forming a sulphide in presence of acid.

*2. With ammonium sulphide they give a black precipitate, soluble in hydrogen chloride.

To the clear liquid obtained in the last experiment add solution of ammonium hydrate (which will combine with the hydrogen sulphide, forming ammonium sulphide). A black precipitate of iron protosulphide will be formed, which will readily dissolve on addition of a few drops of dilute hydrogen chloride.

*3. With potassium hydrate they give a white precipitate, quickly turning black and then reddish brown.

Pour into a test-tube a few drops of solution of potassium hydrate, add a little water, and then a drop or two of the solution of iron protosulphate. A grayish white flocculent precipitate of iron protohydrate (FeH_2O_2) will be formed, which, if the tube is shaken for half a minute, will rapidly become green, then black, and be finally converted into a reddish brown perhydrate (FeH_3O_3), by absorbing oxygen from the air.

*4. With potassium ferrocyanide they give a white precipitate, quickly turning blue.

Pour into another test-tube a little solution of potassium ferrocyanide, add water, and then a drop of the solution of

iron protosulphate. A precipitate will be formed of iron protoferrocyanide, which is at the first moment nearly white, but rapidly changes to deeper and deeper shades of blue, when the test-tube is shaken, or when the solution is poured backwards and forwards several times from one test-tube to another. This change of colour is due to its conversion by the action of the oxygen of the air into iron per-ferrocyanide, or Prussian blue.

***5. With potassium ferricyanide they give a deep blue precipitate at once.**

Repeat the last experiment, using potassium ferricyanide¹ instead of ferrocyanide. A deep blue precipitate of iron ferricyanide will be at once formed, and will undergo no further change in the air. This forms the paint called 'Turnbull's blue.'

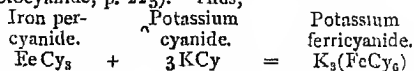
***6. With potassium thiocyanate (or sulphocyanate) they give no change of colour or precipitate.**

To some solution of potassium thiocyanate diluted with water add a drop or two of the solution of iron protosulphate. No change will take place at first in the solution, since iron proto-thiocyanate is colourless; but on shaking the test-tube the liquid will become light red, and eventually of the colour of dark sherry. The appearance of this red colour is an extremely delicate test for iron persalts, as will be seen, p. 404.

***7. Heated in a borax bead they colour the bead yellow in the oxidising flame, dull green in the reducing flame.**

Form a borax bead in the usual way (p. 100) and add to it a minute quantity of powdered iron protosulphate. Heat the bead again, holding it near the tip of the blue flame until the iron salt is dissolved, then bring it into the oxidising flame and hold it there steadily for a few seconds. On withdrawing it from the flame, you will find that (if the right proportion of iron

¹ Potassium ferricyanide is a salt obtained by the combination of iron percyanide with potassium cyanide (just as the ferrocyanide is formed by taking iron protocyanide, p. 223). Thus,



Practically it is prepared by the action of chlorine upon potassium ferrocyanide.

has been taken) it is orange-coloured while hot, becoming light yellow as it cools. In the next place, heat it in the reducing flame for half a minute; its colour will now be found to have changed to a dull green (like that of bottle-glass), which becomes paler on cooling.

Properties of Iron persalts (Ferric salts).

Pour into a test-tube the solution of iron persulphate prepared already; notice that it has a yellow colour, while the solution of the protosalt was nearly colourless; add 30 c.c. of water, and examine portions of the solution with the same tests as those applied to the proto-salts, which may be applied in the usual way to portions of the solution, since iron persalts are not altered in the air.

***1. With hydrogen sulphide they give a white, milky precipitate of sulphur.**

[The precipitate forms more quickly if the solution is warmed.]

This is owing to their reduction to protosalts; the hydrogen of the hydrogen sulphide combining with some of the non-metallic radicle (in this case the sulphate radicle), while its sulphur is separated¹.

***2. With ammonium sulphide they give a black precipitate.**

Add ammonium sulphide to another portion of the solution (which must be neutralised previously with ammonia, if it is acid). A black precipitate of iron protosulphide will be formed, soluble (with the exception of a little sulphur which may separate) in dilute hydrogen chloride.

***3. With potassium hydrate they give a reddish-brown precipitate.**

This consists of iron perhydrate, and is unaltered when shaken up with air.

***4. With potassium ferrocyanide they give a deep blue precipitate.**

This consists of 'Prussian blue,' the formation of which has been already mentioned, p. 223.

¹ $2 \text{Fe}_2(\text{SO}_4)_3 + 2 \text{H}_2\text{S} = 4 \text{FeSO}_4 + 2 \text{H}_2\text{SO}_4 + \text{S}_2$

5. With potassium ferricyanide they give no precipitate, the liquid turning brown.

[If the solution of potassium ferricyanide has been made for some time, it is liable to contain a trace of ferrocyanide, and then the solution becomes green instead of brown.]

*6. With potassium thiocyanate they give a dark red liquid.

This should be tried, with one (or at most two) drops of the solution of the iron persalt in order to prove the delicacy of the test.

*7. Heated in a borax bead they give the same results as the protosalts.

Conversion of salts of the one series into those of the other.

A. Protosalts into persalts.

The principle on which this may be done has already been explained, p. 400: and one mode of effecting it, *viz.* by hydrogen nitrate, has been employed. Besides oxygen, however, other substances which have an affinity for hydrogen may be employed to withdraw it, such as chlorine. In this case the change is, by analogy, still termed an 'oxidation.'

Pour off the remainder of the solution of iron protosulphate into another test-tube (keeping back the undissolved iron), add a few drops of solution of chlorine, and warm the mixture¹. The solution will now give the characteristic reactions of iron persalts, and portions of it should be examined by tests 4 and 6.

B. Persalts into protosalts.

In this case we have to withdraw a portion of the non-metallic radicle from the molecule of persalt. This may be done by various 'reducing' agents (for instance, hydrogen sulphide, as in expt. 1, p. 403), but hydrogen in the nascent state is one of the best for the purpose.

Add a few drops of dilute hydrogen sulphate to the remainder



of the solution of iron persulphate, place a fragment of granulated zinc in the solution, and lay a bit of paper or card on the mouth of the tube, to exclude air. Hydrogen will be evolved by the action of the zinc on the acid, and the solution will gradually lose its colour¹, and will give the reactions of iron protosalts, *viz.* a deep blue precipitate with potassium ferricyanide, and a colourless solution with potassium thiocyanate².

Additional Experiments.

1. Formation of ink.

Dissolve about half a gramme of iron protosulphate in 10 c.c. of water, and add a few drops of solution of iron perchloride (to ensure the presence of a persalt), and then a little infusion of gall nuts or solution of hydrogen gallate (gallie acid). A bluish black precipitate of iron gallate will be formed, which will remain in suspension for a long time, owing to its finely divided state. Ordinary writing ink is thus made, a little gum being added to prevent the subsidence of the precipitate.

2. Passive state of iron.

This is the name given to that condition of iron in which it is unacted on by strong hydrogen nitrate, probably owing to the presence of a thin film of oxide upon its surface (compare the protection of lead by a film of carbonate from the action of water, p. 349).

Pour about 2 c.c. of *strong* hydrogen nitrate (see note³) into a test-tube and put into it a strip of sheet iron or a piece of iron wire, thoroughly cleaned from rust with emery-paper. There will be a momentary action only, a few bubbles of gas being given off, and the iron may then remain for any length of time quite unacted on, and with its surface apparently bright. But if a few drops of water are added, a violent action begins at once, and the iron dissolves, with a rapid evolution of nitrogen oxides.

¹ $\text{Fe}_2(\text{SO}_4)_3 + \text{H}_2 = 2 \text{FeSO}_4 + \text{H}_2\text{SO}_4$

² The presence of the zinc salt will not interfere with these reactions, if the solution contains hydrogen sulphate.

³ The acid must not be of lower density than 1.35. The strong common acid, such as is used for Grove's battery, will do. If this is not at hand, add to the ordinary laboratory acid about half its volume of strong hydrogen sulphate, which will concentrate it by withdrawing water. The mixture should be cooled before the iron is put in.

Properties of Steel.

1. Annealing of steel.

Take a piece of thick watch-spring, or clock-spring, about 1 cm. broad and 10 or 12 cm. long, heat the whole of it to redness in the flame of a Bunsen's burner, and allow it to cool slowly, withdrawing it by degrees from the flame, in the same manner as in annealing glass, p. 27. It will be found, when cool, to have lost its elasticity almost entirely, being pliable enough to be bent into any shape, and soft enough to be pretty easily scratched with a file.

2. Hardening of steel.

Straighten the piece of steel which was just now annealed, heat it again to a uniform redness in the flame of a Herapath's blowpipe, and plunge it quickly into a jug of cold water. This sudden cooling will be found to have had the effect of making it extremely hard and brittle, so that no file will scratch it, and a bit may be broken off the end almost as easily as if it was glass. It is even harder than glass, for its edge will make a scratch on a piece of glass.

3. Tempering of steel.

It has been seen that steel, if heated to redness and cooled very slowly, becomes soft. If, however, it is only heated *slightly* it loses no more than a portion of its hardness; and the amount lost depends entirely upon the temperature to which it has been raised. This is the principle of the process of 'tempering' steel; the temperature being usually judged rather roughly by observing the colour of the film of iron oxide formed in consequence of the heat. A yellow colour implies a very thin film (and a temperature of about 250°), and a blue colour denotes a thicker one (and a temperature of about 300°); and thus, by watching for the appearance of a particular colour and stopping the rise in temperature directly it appears, any desired degree of hardness may be obtained. To illustrate this,—

Take the strip of steel which has just been hardened, lay it flat upon a piece of board and rub it gently with a piece of moistened whetstone (or with a bit of wood dipped in fine emery made into a paste with water) until it becomes quite bright. Now lay it upon a strip of sheet iron and heat it again very carefully, holding it at some distance above the flame and moving it to and fro, so as to heat it uniformly. The surface of the steel will soon begin to show the same succession of tints as the iron in expt. 1, p. 397, passing from yellow to orange and blue. When it has just reached this latter tint, plunge it into cold water, to stop any further action

of the heat. You will now find that it has regained in a great measure the properties of the original watch-spring; that it is stiff and elastic, and that its surface can be filed away, though with difficulty, and much to the damage of the file. If the application of heat had been stopped when the surface became straw-yellow, the hardness would have been less reduced, and the temper would have been such as is required for razors and tools for cutting steel.

4. Relation of iron and steel to magnetism.

Iron is the most strongly magnetic of all bodies; i.e. it is attracted strongly when a magnet is held near it. This is due, in fact, to its becoming a magnet itself, with poles opposite in kind to those of the magnet which causes or 'induces' them.

Support a strip of sheet iron, 6 or 7 cm. long and 1 cm. broad, vertically in a Bunsen's holder, and bring close to the upper end of it one pole (e.g. the N.-seeking, or marked, pole) of a small strong horse-shoe magnet. The lower end of the strip of iron will now show magnetic properties, and will attract a short bit of wire¹ or a small iron nail held near it. This in its turn will become a magnet, and will attract another bit of wire, and thus several may be hung from the strip of iron. But as soon as the inducing magnet is withdrawn, nearly all the magnetic properties of the iron cease to show themselves, and the bits of wire drop off.

Steel, on the contrary, is not only magnetic in the above sense, but is (especially when hardened) capable of being magnetised permanently by several methods, of which the following is the simplest.

Lay the strip of steel, which was tempered just now (or a similar piece of watch-spring), on the table, and hold it down by pressing the forefinger on its centre. Bring down the N.-seeking pole of the horse-shoe magnet vertically on the middle of the strip, and move it to one extremity, rubbing it rather strongly upon the surface of the steel. Then bring it back at a distance through the air to the centre of the strip as before, and again pass it along to the extremity. Repeat this about six times, and then rub the other half of the strip with the *other* (i.e. the S.-seeking pole) in the same way and for the same number of times. Remember to move the pole along the strip always in the same direction, *viz.* from the centre to the end, and to bring back the magnet to the centre in a wide curve

¹ A dozen, or more, bits of thin annealed non wire, about 1 cm. long, should be cut.

through the air, otherwise the magnetism already imparted will be weakened.

The bit of steel will now be found to be a permanent magnet, that end being the N.-seeking pole which was rubbed with the S.-seeking pole of the horse-shoe.

(a) Touch some small bits of iron wire (or nails) with it: they will be strongly attracted.

(b) Hang it in a small stirrup of paper, suspended by a fine bit of cotton (or a long hair) from a Bunsen's holder: it will range itself N. and S. like the compass needle, and its N.-seeking pole will be repelled by the N.-seeking pole of the horse-shoe magnet (the other pole of the horse-shoe being kept out of the way as much as possible); whereas if a strip of sheet iron is hung in the same way both ends will be attracted indifferently by the magnet.

(c) Lay it flat on the table, place a sheet of paper upon it, and scatter some iron filings upon the paper; then tap the paper so as to allow the filings to arrange themselves in obedience to the magnet underneath. They will place themselves in regular curves, marking the direction of the lines of magnetic force.

2. COBALT.

[Symbol of atom, Co.

Weight „ 59 hydrogen-atoms.]

This metal is not of very common occurrence. The chief use of its compounds, *viz.* for imparting a deep blue colour to glass and china, has been illustrated already, p. 309.

Preparation of compounds of Cobalt.

[Typical examples,—Cobalt nitrate,		Formula of molecule.
„ chloride,	Co(NO ₃) ₂	
„ sulphide,	CoCl ₂	
„ protohydrate,	CoS	
„ perhydrate,	CoH ₂ O ₂	
	CoH ₃ O ₃	

A solution of cobalt nitrate (1.5 gm. of the salt dissolved in 30 c.c. of water) may be used.]

1. Cobalt chloride.

Cobalt nitrate is the compound of the metal most generally met with, and from it the chloride can be readily prepared by

heating with hydrogen chloride (a method often employed in analysis to get rid of nitrates when their presence would interfere with the tests).

• Put 5 c.c. of solution of cobalt nitrate into a small porcelain dish, add about 2 c.c. of strong hydrogen chloride, and evaporate it nearly (but not quite) to dryness, in a draught-cupboard. The nitrate will be entirely decomposed with formation of nitrosyl chloride and chlorine¹ (as in the formation of aqua regia) and a deep blue solution of cobalt chloride will be formed. On adding a few drops of water, it will turn red, owing to the formation of a salt containing several molecules of water of crystallisation.

[Keep the solution for a future experiment, p. 411.]

2. Cobalt perhydrate (cobaltic hydrate).

This corresponds to iron perhydrate (expt. 3, p. 403), and is one of the few stable persalts of cobalt. In the case of iron, the protosalts most readily pass into persalts; in the case of cobalt the protosalts do not show much tendency to become persalts unless they are acted on by a powerful oxidising agent, such as a hypochlorite.

Add a little freshly made solution of bleaching powder to some solution of cobalt nitrate in a test-tube. A black precipitate of cobalt perhydrate will be formed, owing to the action of the calcium hydrate and hypochlorite present in the bleaching powder (p. 242)².

If some more solution of bleaching powder is added, and the mixture warmed, oxygen will be given off (as already noticed, p. 243): possibly owing to the formation of a still higher cobalt hydrate (as in the case of chromium, p. 427) and its immediate decomposition into oxygen and cobalt perhydrate.

Properties of compounds of Cobalt.

1. Their solutions, if acid, when tested with hydrogen sulphide, give no precipitate.

Add to a portion of the solution of cobalt nitrate two or

¹ $\text{Co}(\text{NO}_3)_2 + 8\text{HCl} = \text{CoCl}_2 + 2\text{NOCl} + 4\text{H}_2\text{O} + 2\text{Cl}_2$

² $4\text{Co}(\text{NO}_3)_2 + 4\text{CaH}_2\text{O}_2 + \text{Ca}(\text{ClO})_2 + 2\text{H}_2\text{O}$
 $= 4\text{CoH}_3\text{O}_3 + 4\text{Ca}(\text{NO}_3)_2 + \text{CaCl}_2$

three drops of dilute hydrogen chloride and then some solution of hydrogen sulphide. No precipitate will be formed, showing that cobalt cannot, like the metals in Group II, be separated from acid solutions by hydrogen sulphide.

***2. Their solutions, if neutral or alkaline, when tested with ammonium sulphide, give a black precipitate, scarcely soluble in cold dilute hydrogen chloride.**

Test another portion with a drop of solution of ammonium sulphide. A black precipitate of cobalt sulphide will be formed. Add to this 1 or 2 c.c. of dilute hydrogen chloride; the precipitate will scarcely dissolve, even when heat is applied. If, however, two or three drops of strong hydrogen nitrate are added (so as to form aqua regia) the cobalt sulphide will be decomposed and dissolved (except, possibly, a slight white residue of sulphur). Observe that, though the addition of a very little hydrogen chloride was sufficient to prevent the formation of the sulphide (in expt. 1), yet a much larger quantity failed to dissolve it when once formed¹.

[This is the basis of a method of separating cobalt (and nickel) from the other metals of this group which form sulphides readily soluble in cold dilute hydrogen chloride.]

***3. With potassium hydrate they give a light bluish precipitate, turning brown on boiling.**

Test another portion with solution of potassium hydrate. A light blue precipitate, consisting of a basic cobalt salt, will be formed; which does not dissolve in excess of the precipitant, but becomes reddish brown when the solution is boiled for a minute or two, owing to its conversion into cobalt protohydrate ($\text{Co H}_2\text{O}_2$). This change is very slow unless an excess of potash is present.

***4. Heated in a borax bead they give a deep blue transparent bead, both in the oxidising and reducing flames.**

This may be tried in the usual way, as directed on p. 100.

¹ Compare what was noticed in the case of lead sulphate (p. 348).

Additional Experiments.

1. Change in colour of Cobalt chloride when heated.

Cobalt chloride separates from its solutions in red crystals containing six molecules of water united with each molecule of the salt. These when slightly heated give up their water of crystallisation, leaving the anhydrous salt, which is blue. But this latter substance quickly absorbs water again, becoming once more the pink hydrated salt.

Take the pink solution of cobalt chloride already prepared, p. 409, and trace letters with it on a sheet of writing paper with a glass rod or a camel's-hair brush: then allow them to dry in the air. The letters will now be only faintly visible from their pink colour (if pink paper is used they will be scarcely visible at all). Now warm the paper very gently by holding it before a fire or at some distance over a lamp. As it gradually gets warm, the letters will appear in deep blue, owing to the loss of water of crystallisation as above explained. Discontinue the heating as soon as the above result is obtained (otherwise the salt may be decomposed entirely), and breathe upon the paper or hold it in a current of steam from a kettle, or elbow-tube attached to a flask of boiling water. Water will be again absorbed by the cobalt chloride, and the original faint pink salt will be obtained, the letters almost disappearing.

This illustrates what was formerly called a 'sympathetic ink,' in which secret messages could be written which only appeared when warmed¹.

*2. Preparation of Cobalt-potassium nitrite.

Add to about 2 or 3 c.c. of the solution of cobalt nitrate five or six drops of hydrogen acetate and then a little solid potassium nitrite (about as much as will lie on the end of a spatula). Warm the liquid gently (but do not boil it), and set it aside in a warm place for a day. A bright yellow precipitate of cobalt-potassium nitrite (the paint known as 'cobalt yellow') will gradually form, and the whole of the cobalt will eventually though slowly be separated from solution.

¹ Paper or card, covered with cobalt chloride, serves as a rough hygrometer; remaining pink as long as the air is nearly saturated with water vapour, but turning blue when the air is comparatively dry.

It may be interesting to notice that if three or four drops of a very concentrated solution of cobalt chloride are diluted with 4 or 5 c.c. of alcohol, a liquid is obtained which is red when cold, but turns deep blue when the tube containing it is put into hot water.

This illustrates a method (probably the best) of separating cobalt from nickel, since nickel forms no similar insoluble double salt under the above conditions.

3. NICKEL.

[Symbol of atom, Ni.

Weight „ 59 hydrogen-atoms.]

The close analogy between nickel and cobalt as regards their ores, their physical properties, the weight of their atoms, and the compounds they form, should be studied with care. If any metallic nickel is at hand, it should be tested with a magnet. It will be found to be attracted by the magnet, like iron, but not so strongly.

Nickel is now used in large quantities for coating other metals, such as iron, to preserve them from rust. For this purpose it is deposited on their surfaces by decomposing a solution of nickel-ammonium sulphate by means of an electric current, as silver is deposited in electroplating. This may be illustrated on a small scale as follows:—

Clean a strip of copper, about 10 cm. long and 1 cm. broad, with emery-paper, and bend it into the form shown by the thin line in fig. 96, the end *a* forming a clip in which is to be placed a strip of zinc of the same breadth and 4 or 5 cm. long, bent as shown by the thick line in the figure.



Fig. 96.

Dissolve 2 grms. of nickel sulphate in 20 c.c. of water, and add to the solution 10 c.c. of solution of ammonium chloride (the ordinary laboratory solution). In this way the double salt, nickel-ammonium sulphate, $\text{Ni}(\text{H}_4\text{N})_2(\text{SO}_4)_2$, is formed, which is found to yield the best deposit by electrolysis. Pour the solution, which should be just neutral, into a small porcelain dish, and put into it the strip of copper in the position shown in the above figure, so that the horizontally-bent portion of the zinc dips below the surface of the liquid: then leave it undisturbed for half an hour. A galvanic action will be

set up between the zinc and the copper, and the current in passing through the solution will decompose it; metallic nickel being deposited as a steel-gray, firmly-adherent film on the copper.

Properties of compounds of Nickel.

	Formula of molecule.
[Typical examples,—Nickel sulphate,	NiSO_4
„ sulphide,	NiS
„ hydrate,	NiH_2O_2

A solution of nickel sulphate containing 1 grm. dissolved in 30 c.c. of water may be used.]

The following experiments may be made in the same way as already directed in the case of cobalt; the resemblances and differences in the properties of the salts of the two metals being put down side by side in parallel columns in the note-book.

*1. Their solutions, if acid, when tested with hydrogen sulphide, give no precipitate.

*2. Their solutions, if neutral or alkaline, when tested with ammonium sulphide, give a black precipitate of nickel sulphide, scarcely soluble in cold dilute hydrogen chloride¹.

*3. With potassium hydrate they give a light green precipitate, unaltered on boiling.

This precipitate consists of nickel protohydrate (not, as in the case of cobalt, of a basic salt).

*4. Heated in a borax bead they colour the bead brownish red in the oxidising flame, gray and turbid in the reducing flame.

This must be carefully distinguished from the results obtained with manganese compounds. The bead obtained with the latter is violet, and loses its colour but does *not* become turbid in the reducing flame.

¹ This precipitate of nickel sulphide is very slightly soluble in ammonium sulphide, so that on filtering liquids containing nickel sulphide in presence of excess of ammonium sulphide the filtrate has a characteristic dark brown colour. The traces of nickel thus dissolved may be separated by evaporating the solution until the excess of ammonium sulphide has been decomposed, and then filtering again.

It may be worth notice that the green colour of a solution of nickel sulphate is almost exactly complementary to the red colour of a solution of cobalt nitrate. Each solution, in fact, absorbs just those rays which the other can transmit: so that when a test-tube containing a solution of one of the above salts is held behind a test-tube containing a solution of the other salt, if the strengths of the solutions are properly adjusted, very little light survives the absorptive power of both of them: only a dusky brown tint appearing in the transmitted beam. If the solutions are very concentrated no light will get through at all.

4. MANGANESE.

[Symbol of atom, Mn.

Weight „ 55 hydrogen-atoms.]

Compounds of Manganese.

[Typical examples,—Manganese dioxide,	Formula of molecule.
„	MnO_2
„	protosulphate, MnSO_4
„	protochloride, MnCl_2
Potassium manganate,	K_2MnO_4
„	permanganate, KMnO_4]

Nearly all the compounds of manganese are obtained from the dioxide, which forms the very abundant mineral called Pyrolusite. It can be made both (a) to give up oxygen (and thus form salts related to lower oxides), and (b) to combine with more oxygen (and thus form compounds corresponding to higher oxides).

1. Decomposition of Manganese dioxide by heat.

Place a little dry manganese dioxide in a small test-tube and heat it in a Bunsen's burner as strongly as possible. It will, at a red heat, give off a portion (one-third) of the oxygen it contains, leaving a dull reddish residue consisting of a lower oxide of manganese¹. The presence of oxygen in the tube may be proved by a glowing cedar *pill* in the usual way.

¹ $3\text{MnO}_2 = \text{Mn}_3\text{O}_4 + \text{O}_2$

This reaction is of interest, as showing the method by which oxygen was formerly obtained on a large scale, before potassium chlorate could be cheaply obtained.

2. Decomposition of Manganese dioxide by hydrogen sulphate.

Mix a little manganese dioxide with 2 or 3 c.c. of strong hydrogen sulphate in a test-tube, and heat the mixture cautiously. An effervescence will soon commence, owing to the evolution of oxygen, which may be tested for in the usual way. In this reaction one-half of the total oxygen contained in the manganese dioxide is given off, the rest uniting with the hydrogen of the acid; manganese protosulphate is also formed¹.

If the mixture is left to cool, and then 5 or 6 c.c. of water added, a light pink solution of manganese protosulphate will be obtained. It is, however, contaminated with iron protosulphate (since Pyrolusite always contains iron oxide), from which there is some difficulty in freeing it entirely: the best mode is to evaporate the liquid to dryness and heat the residue to full redness, when the iron protosulphate is decomposed (p. 398), while the manganese salt remains unaltered and can be dissolved out by water.

3. Preparation of Manganese protochloride.

Place 0.5 grm. of manganese dioxide in a porcelain dish, add 6 or 7 c.c. of strong hydrogen chloride, and heat the mixture gently on a sandbath, taking great care that none of the chlorine evolved escapes into the room. The reaction has been already explained under CHLORINE, p. 231. The oxygen of the manganese dioxide is not, in this case, evolved as gas, but combines with the hydrogen of the hydrogen chloride, forming water. Part of the chlorine unites with manganese to form manganese protochloride, while the rest is evolved as gas.

When all the black oxide has disappeared, evaporate the liquid to complete dryness, and heat the light pink residue

¹ $2 \text{MnO}_2 + 2 \text{H}_2\text{SO}_4 = 2 \text{MnSO}_4 + 2 \text{H}_2\text{O} + \text{O}_2$

Thus more oxygen is obtainable from a given weight of manganese dioxide by this reaction than by simply heating the substance. It will be useful to calculate the volume of oxygen obtainable from, say, 10 grms. of the dioxide by each of the two methods.

rather strongly (but not quite to redness), in order to decompose or volatilise any iron chloride which has been formed, owing to the presence of iron as an impurity in the manganese dioxide. Warm the residue, when cool, with 20 c.c. of water, filter the solution and use it in the following experiments.

Properties of Manganese protosalts.

***1. Their solutions, tested with ammonium sulphide, give a dull pink-coloured precipitate.**

Test a portion of the solution of manganese protochloride with a drop or two of solution of ammonium sulphide. This will produce a pink¹ precipitate of manganese sulphide, readily soluble on addition of a few drops of dilute hydrogen chloride.

***2. With potassium hydrate they give a grayish precipitate, soon turning brown.**

Test another portion with a drop of solution of potassium hydrate. A nearly white precipitate of manganese protohydrate (MnH_2O_2) will be formed, which will soon become brown on agitation, passing into the perhydrate (MnH_3O_3) owing to absorption of oxygen from the air.

***3. Heated in a borax bead they colour the bead violet in the oxidising flame, but it loses all colour in the reducing flame.**

Make a borax bead, add to it a minute quantity of manganese dioxide, and heat it in the oxidising flame of the blowpipe. The bead will be coloured violet, but when heated for a short time in the reducing flame, it will become colourless. The reason of this has been already explained, p. 102.

***4. Heated in a bead of sodium carbonate they colour it bluish green.**

Make a bead of sodium carbonate (p. 309), add to it a trace of manganese dioxide, and heat it in the oxidising flame. The opaque bead will, when cold, be of a bluish green colour. This is due to the formation of sodium manganate (analogous

¹ If any iron salt is present, the precipitate will be dark in colour. The solution of manganese protochloride must be evaporated to dryness and ignited again more strongly, to decompose the last traces of iron salts.

to potassium manganate), which will be prepared in the next experiment.

Preparation of Potassium manganate.

We have in this case an example of the way in which manganese dioxide combines with more oxygen to form an electro-negative radicle (MnO_4), somewhat analogous to the sulphate radicle (SO_4). This takes place when it is heated with an oxidising substance, such as a chlorate, in presence of a base, such as potassium hydrate, which can combine with the radicle formed.

Make a mixture of 2 grms. of manganese dioxide with 1.5 gm. of potassium chlorate, and place it in an iron capsule, or spoon. Dissolve 3 grms. of potassium hydrate in 2 c.c. of water, and add the solution to the mixture in the spoon. Stir the whole together, and evaporate it to dryness over the lamp, stirring it, as it froths up, with an iron wire; then heat the dish nearly to redness, and keep it at that temperature for two or three minutes¹. The dark green, semi-fused mass which is formed consists of potassium manganate, and was formerly called 'mineral chameleon,' from the changes of colour which its solution undergoes, as will be presently observed.

Preparation of Potassium permanganate.

This is obtained by the decomposition of the manganate, which shows a great tendency to split up into a compound containing more oxygen, *viz.* a permanganate, and a compound containing less oxygen, such as manganese dioxide or protoxide (compare the decomposition of chlorates, p. 249, note).

Grind some of the potassium manganate, obtained in the last experiment, to fine powder, place a little of it (not more than will lie on the end of a penknife) in a test-tube and add about 10 c.c. of cold water. The salt will readily dissolve, forming a dark green liquid.

¹ $3\text{MnO}_2 + 6\text{KHO} + \text{KClO}_3 = 3\text{K}_2\text{MnO}_4 + \text{KCl} + 3\text{H}_2\text{O}$

(a) Pour about 1 c.c. of this solution into another test-tube, and add enough water to nearly fill the tube. The colour of the liquid will (more or less quickly, according to the amount of free alkali present) change first to a dusky neutral tint, and then to a fine purple, owing to formation of potassium permanganate¹.

(b) Pour 4 or 5 c.c. of the solution into another test-tube, and heat it to boiling. The change of colour will be much quicker in this case, and a flocculent brown precipitate of manganese dioxide, or rather, the corresponding hydrate (MnH_2O_4), will be formed.

(c) Add to the remainder of the solution a few drops of dilute hydrogen sulphate. The formation of the purple potassium permanganate will be immediate in this case; no precipitate occurs, since manganese protosulphate is produced and remains in solution². Dilute the liquid with 30 c.c. of water, observing how slightly the intensity of the rich purple colour is lessened by dilution, and keep it for use in the next experiments.

Properties of the Permanganates.

These salts are chiefly remarkable for the readiness with which they give up oxygen, passing (when an acid is present) into the condition of colourless manganese protosalts. Hence they are much used as oxidising agents in the laboratory, and also on the large scale as disinfectants ('Condy's fluid' being a solution of sodium permanganate). To illustrate this,—

(a) Add to a portion of the solution of potassium permanganate (containing free hydrogen sulphate) a few drops of solution of hydrogen sulphite³. The purple colour will immediately disappear, the permanganate giving up oxygen to the hydrogen sulphite, to form a sulphate⁴.

(b) Add to another portion about one-third its volume of

¹ $3 \text{K}_2\text{MnO}_4 + 4 \text{H}_2\text{O} = 2 \text{KMnO}_4 + 4 \text{KHO} + \text{MnH}_2\text{O}_4$

² $5 \text{K}_2\text{MnO}_4 + 4 \text{H}_2\text{SO}_4 = 4 \text{KMnO}_4 + 3 \text{K}_2\text{SO}_4 + \text{MnSO}_4 + 4 \text{H}_2\text{O}$

³ If this is not at hand, a freshly-made solution of sodium sulphite, acidified with hydrogen sulphate, may be used.

⁴ $2 \text{KMnO}_4 + 5 \text{H}_2\text{SO}_4 = \text{K}_2\text{SO}_4 + 2 \text{MnSO}_4 + 2 \text{H}_2\text{SO}_4 + 3 \text{H}_2\text{O}$

dilute hydrogen sulphate, and six or eight drops of solution of ammonium oxalate, and warm it. The liquid will gradually become brown and finally colourless; the oxalate being oxidised to carbon dioxide¹ (compare the reaction of oxalates with manganese dioxide, p. 220).

(c) Add to another portion a few drops of a solution of iron protosulphate. The purple colour will disappear; the iron protosalt being oxidised to a persulphate. This is the basis of a process for determining the value of iron ores.

(d) Put about 200 c.c. of rain-water (or water from a stagnant ditch²) into a flask, add 5 c.c. of dilute hydrogen sulphate and about three drops of the solution of permanganate (not more than sufficient to colour the liquid decidedly pink); then leave it to stand for an hour or so. If the water contains organic matter (or nitrites formed by its oxidation), this will be oxidised (burnt, as it were) by the permanganate, and the pink colour will disappear. This illustrates the principle of a process for testing the wholesomeness of water to be used for drinking.

Additional Experiment.

Reduction of Permanganates to Manganates.

A comparison of the formulæ of the molecules of potassium permanganate (KMnO_4) and potassium manganate (K_2MnO_4) will show that the latter contains more potassium in proportion to the amount of the other radicle than the former³.

You have seen in expt. c., p. 418, that the addition of an acid to potassium manganate withdraws some of the potassium and causes the formation of a permanganate. Now it is easy, by reversing the conditions, *i. e.* by adding an alkali to potassium permanganate, to effect the reverse change and reduce it to a manganate.

¹ $2\text{KMnO}_4 + 3\text{H}_2\text{SO}_4 + 5\text{H}_2\text{C}_2\text{O}_4 = \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 8\text{H}_2\text{O} + 10\text{CO}_2$. This reaction is used in volumetric analysis for determining the strength of a solution of potassium permanganate; a known weight of hydrogen oxalate being dissolved in water, hydrogen sulphate added, and the solution of permanganate dropped in carefully as long as the purple colour is destroyed.

² If no such water is at hand, bruise a leaf in a mortar, and boil it with a little water for half a minute; add 2 or 3 c.c. of the liquid to 200 c.c. of ordinary water.

³ Compare the difference in the composition of the ferrocyanides (*e. g.* K_4FeCy_6) and ferricyanides (*e. g.* K_3FeCy_6).

Add about 3 grms. of solid potassium hydrate to 3 or 4 c.c. of the solution of potassium permanganate, and warm the mixture. The purple colour will soon change to a dark neutral tint, and finally to a deep green, proving that a manganate has been formed¹.

5. CHROMIUM.

[Symbol of atom, Cr.

Weight „ 52.5 hydrogen-atoms.]

Preparation of compounds of Chromium.

Chromium, like manganese, forms several distinct classes of compounds, in some of which (*e.g.* chromium sulphate) it is present as an electro-positive radicle, or metal, while in others (*e.g.* potassium chromate) it forms part of an electro-negative radicle [CrO_4].

A. Chromium Salts.

	Formula of molecule.
[Typical examples,—Chromium sesquioxide,	Cr_2O_3
„ sesquichloride,	Cr_2Cl_6
„ -potassium sulphate, Cr K(SO ₄) ₂	
(‘chrome alum’)	

For the following experiments a solution of chromium-potassium sulphate (3 grms. of the salt dissolved in 30 c.c. of water) may be used.]

The most stable and best-known series of these is that of the chromium persalts, or sesquisalts, corresponding to the iron persalts.

1. Chromium sesquioxide.

Add some solution of ammonium hydrate to about 8 or 10 c.c. of the solution of chromium-potassium sulphate. A dull bluish gelatinous precipitate of chromium hydrate (CrH_3O_3) will be formed. Add sufficient ammonium hydrate to make the

¹ $4\text{KMnO}_4 + 4\text{KHO} = 4\text{K}_2\text{MnO}_4 + 2\text{H}_2\text{O} + \text{O}_2$

The reaction really involves a change in the valency of the manganese; the permanganates being related to a hitherto-unisolated manganese heptoxide (Mn_2O_7), while the manganates are similarly related to an oxide having the formula MnO_3 (analogous to sulphur trioxide, SO_3).

liquid smell slightly of it, showing that it is in excess; warm the mixture, to promote the separation of the precipitate; then pour the whole on a filter, wash the precipitate thoroughly, and put the filter containing it to dry in a porcelain dish on the sand-bath. Observe that it shrinks in bulk considerably in drying, especially if the temperature is pretty high, giving off water and becoming chromium sesquioxide¹, of an olive-green colour, sometimes used as a paint. Reserve it, when dry, for future experiments, p. 422.

2. Chromium-potassium oxide.

To another portion of the solution of chrome alum add, drop by drop, solution of potassium hydrate, shaking the mixture after each addition. The chromium hydrate, which is at first precipitated, will readily dissolve in excess of potassium hydrate, forming a deep green solution of chromium-potassium oxide². [Be careful to add no more potassium hydrate than is required to dissolve the precipitate.] Boil this fluid for two or three minutes; it will become turbid, and eventually the whole of the chromium will be reprecipitated as hydrate, in a form in which it is no longer soluble in potassium hydrate.

Tests for Chromium salts.

***1. Their solutions, tested with ammonium sulphide, give a dull bluish precipitate.**

Test a portion of the solution of chromium-potassium sulphate with a few drops of ammonium sulphide. A light bluish-gray gelatinous precipitate will be formed, which consists of chromium hydrate, and not chromium sulphide, as might be expected; since the latter is decomposed in presence of water, with evolution of hydrogen sulphide³.

***2. With potassium hydrate they give a dull bluish**

¹ $2\text{CrH}_3\text{O}_3 = \text{Cr}_2\text{O}_3 + 3\text{H}_2\text{O}$

² $\text{CrH}_3\text{O}_3 + \text{KHO} = \text{KCrO}_3 + 2\text{H}_2\text{O}$

The reaction is very similar to that which occurs between arsenic trioxide and potassium hydrate, p. 367: and the compound should perhaps be called potassium chromite (analogous to potassium arsenite, KAsO_2).

³ $\text{Cr}_2\text{S}_3 + 6\text{H}_2\text{O} = 2\text{CrH}_3\text{O}_3 + 3\text{H}_2\text{S}$

precipitate, soluble in excess, but re-precipitated on boiling.

This has been tried already, in the last expt. but one.

*3. Heated in a borax bead they colour the bead bright green both in the oxidising and reducing flames.

This may be tried in the usual way, a very minute quantity (not so large as a pin's head) of chrome alum being used.

This illustrates an important use of chromium compounds, *viz.* in colouring glass and painting on porcelain.

B. Chromates.

	Formula of molecule
[Typical examples,—Potassium chromate,	K_2CrO_4
„ dichromate,	$K_2Cr_2O_7$
Lead chromate,	$PbCrO_4$]

In these chromium forms part of the electro-negative radicle (CrO_4), the analogy of which to the sulphate radicle (SO_4) should be noted. They are related to chromium trioxide (CrO_3), which can be obtained from them, as will be presently proved; and they can be easily obtained by the action of an oxidising agent upon chromium sesquioxide in presence of some basic radicle, *e.g.* potassium or sodium.

1. Potassium chromate.

Take the precipitate of chromium sesquioxide obtained in expt. 1, p. 421, mix it intimately with about the same quantity of potassium nitrate and of sodium carbonate (roughly measured), and fuse the mixture in an ignition-tube. It will turn red, becoming yellow as it gets cooler; the chromium sesquioxide having combined with oxygen and potassium from the potassium nitrate to form potassium chromate¹.

Dip the bulb while still hot into a little water placed in a porcelain dish, when it will crack and the chromates will readily

¹ $Cr_2O_3 + 4KNO_3 = 2K_2CrO_4 + N_2O_4 + N_2O_5$

The above equation does not, of course, express fully what takes place. Some sodium chromate is also formed, and a variable mixture of various nitrogen oxides is given off.

dissolve in the water, forming a yellow solution. Pour this solution into a test-tube, and keep it for use in the next expt.

2. Potassium dichromate.

This salt, as may be seen from the formula of its molecule ($K_2Cr_2O_7$), contains more chromium and oxygen (in fact, the elements of an additional molecule of chromium trioxide) combined with potassium than the chromate ($K_2Cr_2O_4$)¹. This alteration in the proportions of basic and acid radicle is readily effected by withdrawing some of the potassium from the chromate by means of hydrogen sulphate.

Add dilute hydrogen sulphate, little by little, to the yellow solution of potassium chromate obtained in the last expt. At first an effervescence will occur, due to the decomposition of the excess of sodium carbonate used in making the salt; but when an excess of the acid has been added, the colour of the solution will change from yellow to red, potassium dichromate being now formed². This latter salt is much less soluble in water than the chromate, and if the solution is strong or if a saturated solution of potassium chromate is taken, the addition of excess of acid will cause the separation of potassium dichromate as a red crystalline powder.

[Some other chromates, such as lead chromate and silver chromate, have been prepared already.]

Tests for Chromates.

[A solution of potassium chromate, containing 1 gm. of the salt dissolved in 30 c.c. of water may be used.]

*1. Their solutions, if acid, when tested with hydrogen sulphide, give a white precipitate of sulphur, the colour of the liquid becoming green.

Add to some of the solution of potassium chromate an equal volume of dilute hydrogen chloride (observing the change of colour due to the formation of a dichromate, as above explained),

¹ $K_2Cr_2O_7 = K_2Cr_2O_4 + CrO_3$

Compare the composition of sodium diborate, p. 304, and of 'Nordhausen' sulphuric acid, hydrogen disulphate, p. 398, note.

² $2 K_2Cr_2O_4 + H_2SO_4 = K_2Cr_2O_7 + K_2SO_4 + H_2O$

then some solution of hydrogen sulphide, and warm the mixture. A white, milky precipitate of sulphur will be formed, and the red colour of the solution will change to green. This is due to the reduction of the chromate to chromium sulphate, some of its oxygen having united with the hydrogen of the hydrogen sulphide (compare the somewhat analogous reaction of iron persulphate, p. 403).

***2. With lead acetate they give a bright yellow precipitate.**

This consists of lead chromate, which has been already prepared, p. 346.

***3. With silver nitrate they give a purple-red precipitate.**

This has been already applied as a test for silver, p. 326.

***4. Heated in a borax bead they colour the bead bright green in both flames.**

This is the same reaction as that given by chromium salts, p. 422.

Reduction of Chromates to chromium salts.

Chromates, like permanganates, show a great tendency to give up oxygen, and are often used as oxidising agents. One example of this, *viz.* their action on hydrogen sulphide, has been given above. Their conversion into chromium persalts can also be easily effected by boiling their solutions, in presence of an acid, with alcohol; some of the hydrogen of the latter being withdrawn by the oxygen of the chromate, forming water, while a substance called 'aldehyde' is given off¹.

Add to 4 or 5 c.c. of solution of potassium chromate about 1 c.c. of strong hydrogen chloride and 2 c.c. of alcohol, and warm the mixture in a beaker. Vapours of aldehyde will be evolved, easily recognised by their pungent oppressive smell, and the red colour of the solution will change to green, owing

¹ Potassium chromate. Alcohol. Hydrogen chloride. Potassium chloride. Chromium chloride. Aldehyde. Water.
 $2 \text{K}_2\text{CrO}_4 + 3 \text{C}_2\text{H}_5\text{O} + 10 \text{HCl} = 4 \text{KCl} + \text{Cr}_2\text{Cl}_6 + 3 \text{C}_2\text{H}_4\text{O} + 8 \text{H}_2\text{O}$

to the formation of chromium sesquichloride as explained above. After boiling it for a minute, pour off half of the solution into a test-tube.

(a) Add to one portion two or three times its volume of water (to prevent the precipitation of lead chloride), and test it with solution of lead acetate. No yellow precipitate will be formed¹; this shows that no chromate is now present.

(b) To the remainder add solution of potassium hydrate, drop by drop, until it is in excess. The formation of a greenish precipitate, soluble in excess, shows that a chromium salt has been formed.

[Other methods of effecting the same change are,

1. The action of hydrogen sulphite, which is analogous to its action upon permanganates, p. 418.

2. The action of strong hydrogen chloride at a high temperature upon a solid chromate. In this case chlorine is given off (as with manganese dioxide, p. 231); and this process is sometimes used for preparing chlorine.]

Additional Experiments.

1. Preparation of Chromium trioxide.

It has been seen already (expt. 2, p. 423) that when hydrogen sulphate is added to a chromate part of the base is withdrawn, and a dichromate is formed. If, however, a great excess of strong hydrogen sulphate is added, the whole of the base is withdrawn and chromium trioxide is separated². This latter, though soluble in strong as well as in very dilute hydrogen sulphate, is insoluble in slightly dilute acid (containing about 16 per cent. of water), and may thus be almost entirely precipitated.

Dissolve 2 gms. of potassium dichromate in 15 c.c. of water heated in a small beaker. Allow it to cool until crystals just begin to appear, and then place the beaker on a plate (lest it should crack), add 20 c.c. of strong common hydrogen sulphate, and stir with a glass rod. The liquid will, of course, get very hot, and the beaker should be covered with a glass plate or watch-glass, and set aside to cool.

¹ If any yellow precipitate occurs, insoluble on warming the liquid, the reduction is not complete, and the remainder of the solution must be again boiled with addition of a little more alcohol and acid.

² $K_2Cr_2O_7 + H_2SO_4 = K_2SO_4 + CrO_3 + H_2O$

Crimson crystals of chromium trioxide will be gradually deposited; and when they have entirely subsided, the greater part of the liquid should be poured off, and the remaining mixture shaken up and transferred to a funnel in the neck of which a few loose asbestos fibres have been placed to prevent the crystals falling through. The funnel should be covered with a glass plate to prevent absorption of moisture by the trioxide. When the liquid has drained off, the mass of crystals may be scraped out with a glass rod upon a dry porous tile or brick. Cover them with an inverted evaporating dish, and leave them until the liquid has been absorbed as far as possible by the brick. Half an hour will generally be sufficient for this purpose, and as the chromium trioxide is very deliquescent it should be protected as far as possible from the air, and not left longer than is necessary on the brick. When it is dry the following experiments may be tried with portions of it; the remainder, if the crystals are good, may be kept as a specimen in a small stoppered bottle, or in a stout test-tube hermetically sealed by drawing out the upper part of it in the blowpipe flame.

2. Properties of chromium trioxide.

(a) It gives off oxygen when heated.

Place a little chromium trioxide (which should be pretty free from adhering acid) in a small test-tube, supported nearly horizontally, and heat it. The substance will melt, and on being further heated will decompose with incandescence, leaving a green residue of chromium sesquioxide, while oxygen will be evolved, and may be tested for by a glowing splinter of wood.

(b) It oxidises alcohol.

Pour a few drops of strong alcohol into a small wide-mouthed gas-bottle, and shake it up so as to diffuse the vapour; then throw into the bottle some of the chromium trioxide. The latter will be reduced to sesquioxide, the action being occasionally so violent as to set the alcohol on fire.

3. Formation of a higher chromium oxide.

Although chromium trioxide so readily gives up oxygen, yet it is possible to get it to combine with more oxygen. For this purpose a very powerful oxidising agent, hydrogen dioxide, must be used; and the first step will be to prepare a solution of this by acting upon barium dioxide with hydrogen chloride (an action which will be more fully explained under **BARIUM**).

Place a little barium dioxide ¹ (as much as will lie on the end of a

¹ For the method of making this substance see p. 439.

spatula) in a mortar, powder it, if necessary, pour upon it about 7 or 8 c.c. of dilute hydrogen chloride, and grind them together until the peroxide has entirely dissolved, adding a little more acid at once if a strong effervescence, due to escape of oxygen, sets in (a mere slight effervescence may be disregarded). A solution containing hydrogen dioxide will be thus obtained.

(a) Place about half of this solution in a test-tube, and add three or four drops of a solution of potassium chromate acidified with hydrogen chloride. The colour of the solution will change to a deep blue, but in a second or two this will disappear, while oxygen is given off with effervescence, and a pale green solution will be obtained. These changes of colour are due to the formation of a higher chromium oxide, which is very unstable, and decomposes, when hydrogen chloride is present, with formation of oxygen and chromium chloride.

(b) This blue chromium oxide (of which the constitution is uncertain) is much more stable when dissolved in ether. To illustrate this, add to another portion of the solution of hydrogen dioxide sufficient ether to form a stratum about 1 cm. in depth; pour in one or two drops of the solution of potassium chromate, immediately close the mouth of the test-tube with the thumb, and shake the mixture. If it is now allowed to remain undisturbed for a minute, the ether will rise to the surface, forming a magnificent blue stratum, while the liquid below is nearly colourless.

Action of light upon Chromates.

When a soluble chromate is exposed to light in presence of organic matter, it is reduced to an insoluble chromium sesquioxide, which adheres very closely to the substance, and, if the latter is gelatine, renders it quite insoluble also. This fact has lately found very extensive applications in the Autotype, Heliotype, and many other printing processes.

Dissolve 5 grms. of potassium dichromate in 50 c.c. of water¹, and filter the solution into a plate. Float upon it a piece of drawing-paper 10 or 12 cm. square (as directed, p. 327), covering the whole with a larger plate or inverted tray to protect it from the action of light. [It is best, in fact, to make the experiment in a darkened room or at night by candle-light, although the dichromate is not so

¹ If any powdered gum arabic is at hand, it is an advantage to add about 5 grms. of it to the solution of the dichromate. The latter is thus retained more on the surface of the paper and a sharper print is obtained.

sensitive to light as silver chloride.] When it has soaked for five minutes, remove the paper and pin it up to dry in a dark cupboard.

When it is quite dry spread it out flat on a board, and lay upon it a piece of black lace, or a pattern cut out in thick brown or black paper; put over the whole a plate of glass to keep it flat, and expose it to full daylight. The unprotected portions of the paper will soon change in colour from bright yellow to dull brown, owing to the reduction of the dichromate, as above explained. In about half-an-hour's time the print may be taken into a dimly-lighted room, and washed with several changes of warm water. All the unchanged yellow salt will dissolve out, leaving a permanent brown picture on a white ground: the chromium sesquioxide attached to the paper being quite insoluble.

In practice the dichromate is mixed with a warm solution of gelatine or glue, and lampblack is stirred up in the mixture, which is then spread upon paper. After exposure to light, the print is washed as above described, when all the unaltered dichromate, together with the gelatine and lampblack, is removed, leaving the picture in permanent black.

[If it is desired to strengthen the print above obtained, it may, after washing, be soaked for five minutes in a solution of iron protosulphate (2 grms. in 50 c.c. of water). Iron oxide is thus deposited where the chromium oxide exists; and if the print, after another thorough washing, is placed in a solution of potassium ferrocyanide (5 c.c. of the laboratory solution with 20 c.c. of water, and 2 c.c. of dilute hydrogen chloride), a deep blue picture is obtained.]

6. ALUMINIUM.

[Symbol of atom, Al.

Weight „ 27.5 hydrogen-atoms.]

If any metallic aluminium is at hand, its density should be determined by the usual method, p. 51. It will be found to have a comparatively low density (2.5), no greater than that of glass. The action of solvents on it may also be tried. Hydrogen nitrate, whether dilute or strong, will be found to have little or no action on it, even when warmed; dilute hydrogen chloride will dissolve it pretty readily with evolution of hydrogen and formation of aluminium chloride. Potassium hydrate (the ordinary laboratory solution) will be acted on by it even more

readily, hydrogen being evolved and a soluble salt called potassium aluminate (KAlO_2) being formed, which will be further alluded to presently.

Compounds of Aluminium.

[Typical examples,—	Formula of molecule.
Aluminium oxide,	Al_2O_3
Aluminium hydrate,	AlH_3O_3
Aluminium-potassium sulphate, ('potash-alum')	$\text{KAl}(\text{SO}_4)_2, (\text{H}_2\text{O})_{12}$
Aluminium-ammonium sulphate, ('ammonia-alum')	$(\text{H}_4\text{N})\text{Al}(\text{SO}_4)_2, (\text{H}_2\text{O})_{12}$
Potassium aluminate,	KAlO_2]

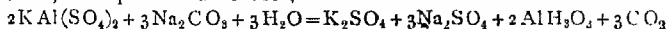
Aluminium seems to form only one series of compounds, comparable with the persalts formed by iron and the other members of this group. Its most important property is that of forming, in association with potassium and the other alkali-metals, double sulphates called 'alums,' which crystallise readily in the form of regular octohedra (as has been proved already, p. 62).

[A solution of alum (either ammonia-alum or potash-alum), containing 5 grms. of the salt in 50 c.c. of water, may be used in the following experiments.]

1. Aluminium hydrate and oxide ('alumina').

Add to about 10 c.c. of the solution of alum half its volume of solution of sodium carbonate, and warm the mixture¹. Carbon dioxide will be given off, and a white gelatinous precipitate of aluminium hydrate will be formed, much resembling hydrogen silicate in appearance. Pour a few drops of the mixture into another test-tube for use in the next expt. Pour the rest on a filter, and wash the precipitate with several changes of water: then dry it by laying the filter containing it in a small dish on a

¹ It might be expected that the double decomposition would result in the formation of aluminium carbonate, but this compound does not appear to exist, and the following equation expresses the actual changes which occur, when potash-alum is used,—



sandbath or on wire gauze. Observe that it shrinks considerably as it gets dry (like chromium hydrate). When it is quite dry, place some of it in a cup of platinum foil (p. 8) and heat it to full redness over a Bunsen's burner. It will contract still more in bulk, giving off the elements of water and becoming aluminium oxide¹.

Moisten the white mass with a *very little* solution of cobalt nitrate, and again heat it for a minute to bright redness. It will be found, on cooling, to have become deep blue; a double oxide (cobalt-aluminium oxide) being formed, which is used as a paint.

2. Potassium aluminate.

Add to the portion of the precipitated aluminium hydrate reserved in the last expt. a few drops of solution of potassium hydrate. The substance will readily dissolve, potassium aluminate being formed², a compound in which aluminium forms part of the electro-negative radicle (compare chromium-potassium oxide, p. 421, and potassium arsenite, p. 367).

Tests for compounds of Aluminium.

*1. Their solutions, tested with ammonium sulphide, give a white precipitate.

Test a portion of the solution of alum with solution of ammonium sulphide, warming the mixture. The grayish-white gelatinous precipitate thus produced consists of aluminium hydrate, since the sulphide (like that of chromium) is not stable in presence of water.

*2. With potassium hydrate they give a white precipitate soluble in excess, but reprecipitated by ammonium chloride.

To another portion of the solution add solution of potassium hydrate, drop by drop. A white gelatinous precipitate of aluminium hydrate will be formed at first, but on addition of more potassium hydrate it will readily dissolve (for the reason

¹ $2 \text{ Al H}_3\text{O}_4 = \text{Al}_2\text{O}_3 + 3 \text{ H}_2\text{O}$

² $\text{K H O}_2 + \text{Al H}_3\text{O}_3 = \text{K Al O}_2 + 2 \text{ H}_2\text{O}$

already explained, p. 430). Divide the solution into two parts:

(a) To one portion add one or two drops of solution of hydrogen sulphide. No precipitate will be produced, since aluminium sulphide is not formed in presence of water.

(b) To the other add about half its volume of solution of ammonium chloride, and warm the mixture; aluminium hydrate will be precipitated.

[These two tests distinguish it from the somewhat similar precipitate formed by adding potassium hydrate to zinc salts, p. 434.]

***3. Heated on charcoal they give a white infusible residue, turning blue when ignited with cobalt nitrate.**

Place a small crystal of alum in a cavity cut in a piece of charcoal, and heat it in the hottest part of the blowpipe flame. The salt will at first swell up like borax, white fumes of ammonium sulphate (if ammonium alum is used) and hydrogen sulphate will then be given off, and finally a white infusible incandescent residue of aluminium oxide will be left on the charcoal. Allow this to cool, then moisten it with a small drop of solution of cobalt nitrate (transferred from the bottle on a glass rod), and ignite it again for several seconds. The mass, when cool, will be found to have acquired a bright blue colour¹, for a reason already explained, p. 430.

Additional Experiments.

1. Formation of 'lakes.'

These are combinations of aluminium hydrate with various colouring matters, for which it has a great affinity.

Make a little solution of cochineal by powdering three or four of the grains of the material, and boiling them with 10 c.c. of water for a minute or two. Filter this from any undissolved particles, and add to it about 5 c.c. of the solution of alum; then add 2 or 3 c.c. of solution of sodium carbonate, boil, and filter the liquid. The aluminium hydrate, precipitated by the sodium carbonate (as already

¹ This reaction, however, is not absolutely characteristic of aluminium, since some silicates, calcium phosphate, and one or two other substances behave in a similar way.

explained, p. 429), will combine with and carry down with it the colouring matter of the cochineal; so that the filtrate will be nearly or quite colourless, while the precipitate on the filter will be pink. This illustrates the preparation of 'carmine lake' used in painting; and various other lakes are made in a similar way from madder, logwood, &c.

3. Use of aluminium salts as 'mordants' in dyeing.

This depends upon the property possessed by aluminium hydrate of attaching itself firmly to the fibre of cloth and calico, as well as of combining with colouring matters, as already shown. Thus it may be employed to bind the two together, as it were; the result being a 'fast' colour, *i.e.* one which cannot be removed from the material by washing.

In order to precipitate the aluminium hydrate on the cloth, the latter is soaked in some readily decomposable salt of aluminium, such as the sulphate or acetate, and left to dry in a warm place. By this means aluminium hydrate is deposited in close contact with the fibre.

Put about 15 c.c. of the solution of alum into a test-tube, and add solution of sodium carbonate, drop by drop, shaking thoroughly after each addition. The precipitate of aluminium hydrate which is at first formed will redissolve, and the addition of sodium carbonate should be continued until a *slight* permanent cloudiness shows itself; when about 1 c.c. of the solution of alum should be added to redissolve this. You have now a solution containing a basic aluminium sulphate which is readily decomposed on boiling, aluminium hydrate being precipitated. [Prove this by pouring off 2 or 3 c.c. of the liquid into another tube and heating it; a white precipitate will be formed.]

Dip one half of a strip of white calico into the solution, and dry it before a fire, or at some distance above a lamp. During the process of drying, the aluminium sulphate is decomposed, aluminium hydrate being deposited in the fibres of the calico. Warm some moderately strong solution of cochineal or logwood in an evaporating dish, immerse the strip of calico, and heat the liquid to boiling for about ten minutes; then take out the calico, and wash it thoroughly in several changes of water. The part of it which was soaked in the 'mordant' solution will be found to be permanently dyed, while all the colouring matter will be washed out of the other portion.

[If a little powdered gum arabic is mixed in a mortar with 2 or 3 c.c. of the solution of aluminium sulphate, and patterns or letters

are drawn upon a piece of calico with a brush or glass rod dipped in it, they will be permanently printed, when treated as above described.]

7. ZINC.

[Symbol of atom, Zn.

Weight „ 65 hydrogen-atoms.]

Properties of the metal.

1. Its fusibility (at 330°) and its oxidability when heated in air have been already noticed in the granulation of the metal (p. 25).

2. Action of heat in altering its tenacity.

Take a strip of sheet zinc about 15 cm. in length, hold it by its extremities and bend it double; notice that it is stiff, and requires some little force to bend it. Now heat it in the middle gently over a lamp, and observe that its pliability is greatly increased. If, however, it is still further heated, it becomes quite brittle as the temperature approaches its melting-point.

Compounds of Zinc.

Formula of molecule.

[Typical examples,—Zinc oxide, Zn O

„ sulphate, Zn SO₄

„ chloride, Zn Cl₂.]

Zinc appears to form only one series of compounds, in which its atom is divalent, like those of cobalt, nickel, and manganese.

*1. Zinc oxide.

Heat a small fragment of zinc on charcoal in the hottest part of the blowpipe flame. It will, when the heat rises to full redness, begin to burn with production of zinc oxide, light flakes of which will be swept away by the current of air, but the greater part will remain on the charcoal, as an incrustation which is yellow while hot, white when cold.

Moisten this incrustation with a small drop of solution of cobalt nitrate on the end of a glass rod, and heat it again before the blowpipe. The mass will now acquire a fine green colour,

a compound of zinc oxide and cobalt oxide being formed, which is used as a paint.

2. Zinc chloride.

3. Zinc sulphate.

The modes of preparing both of these salts have been illustrated already, p. 80, and p. 125.

A solution of one of them will be required in some of the following expts., and should be made, if it is not at hand, by dissolving about 1 gm. of zinc in 10 c.c. of dilute hydrogen chloride, evaporating to dryness to drive off excess of acid, and dissolving the residue of zinc chloride in 30 c.c. of water.

4. Zinc-potassium oxide.

The formation of this substance (which resembles the corresponding chromium compound, p. 421, and aluminium compound, p. 430) by the action of zinc upon potassium hydrate has been illustrated already, p. 165. It is also produced when potassium hydrate is added in excess to a solution of a salt of zinc.

Add to some solution of zinc chloride (or sulphate) a drop (not more) of solution of potassium hydrate. A white precipitate of zinc hydrate (ZnH_2O_2) will be formed. Add more potassium hydrate to this precipitate: it will readily dissolve, zinc-potassium oxide (which should perhaps be called 'potassium zincate') being formed¹.

Tests for compounds of Zinc.

*1. Their solutions, when tested with ammonium sulphide, give a white precipitate.

Test a portion of the solution of zinc sulphate (or chloride) with a drop of solution of ammonium sulphide. A white precipitate of zinc sulphide will be formed, which will readily dissolve on addition of a drop or two of dilute hydrogen chloride.

*2. With potassium hydrate they give a white precipitate, soluble in excess, and not reprecipitated by ammonium chloride.

¹ $\text{ZnH}_2\text{O}_2 + 2\text{KHO} = \text{K}_2\text{ZnO}_2 + 2\text{H}_2\text{O}$

Add to another portion a drop of solution of potassium hydrate. A white precipitate of zinc hydrate will be formed, which, as already seen, will readily redissolve on addition of a few more drops of the solution of potassium hydrate. Divide the clear liquid into two parts :

- (a) To one portion add a drop or two of solution of hydrogen sulphide. A white precipitate of zinc sulphide will be formed.
- (b) To the other portion add about half its volume of solution of ammonium chloride, and warm the mixture : no precipitate will be formed¹.

[Compare the reactions of aluminium salts, p. 431.]

Additional Experiments.

1. Amalgamation of Zinc.

By this is meant the process of covering the metal with a film of mercury, which forms an alloy or 'amalgam' with it. Ordinary zinc is readily acted on by dilute acids, as has been already noticed (p. 80), but this is chiefly due to the presence of particles of carbon, lead, &c., which promote the chemical action by the galvanic current set up between each of them and the zinc. This 'local action,' as it is called, is entirely prevented by covering the zinc with mercury; the latter buries the impurities, so that the acid does not reach them at all.

Put about 20 c.c. of water into a test-tube, add about 1 c.c. of common hydrogen sulphate, and dip into the acid a strip of zinc about 15 cm. long and 1 cm. broad. Bubbles of hydrogen will at once be given off at all parts of the surface of the zinc. Now add about 1 c.c. of solution of mercury perchloride, and mix it thoroughly with the acid by stirring with the strip of zinc. A bright film of mercury will be deposited on the zinc (compare the deposition of mercury on copper, p. 339), and form an amalgam with it; and the evolution of gas will cease entirely. The strip of zinc in this condition is said to be 'amalgamated,' and may be reserved for use in the next experiment.

Another and more usual mode of amalgamating zinc plates for batteries is first to clean the surface of each with dilute acid, as

¹ If the potassium hydrate contains aluminium hydrate, or hydrogen silicate, a precipitate will, of course, be formed. •

above, and then to lay it in a flat plate and pour over it a drop or two of mercury, rubbing the latter all over the surface with a cork. The excess of mercury should then be drained off (and kept in a bottle for this purpose alone), and the zinc plate should be thoroughly rinsed with water.

2. Use of Zinc in galvanic batteries.

This depends upon the readiness with which it is acted on by many substances; the conditions in the usual galvanic batteries being, two metals immersed in a liquid which acts more strongly upon one of them than upon the other.

Put about 50 c.c. of water into a large test-tube, and mix with it 5 or 6 c.c. of common hydrogen sulphate. Take the strip of zinc which you amalgamated just now, and a strip of copper of the same size; put between them a flat bit of cork about 1 cm. thick, so as to keep them parallel but slightly separated, and bind them in this position by string or a couple of small india-rubber bands. Twist tightly round the upper end of each a bit of fine copper wire 18 or 20 cm. long, taking care that these wires do not touch each other in any part. Immerse the strips in the dilute acid in the test-tube, and observe that no action is perceptible on either metal. Now press together the ends of the wires attached to the copper and zinc respectively; bubbles of hydrogen gas will immediately appear on the surface of the copper, while an electric current flows along the wire¹.

The action may be explained as follows:—The molecules of hydrogen sulphate between the zinc and the copper become 'polarised,' *i.e.* arranged in a definite direction (like a row of magnets), their electro-negative radicles pointing towards the zinc; thus,

Zinc plate. $\parallel \text{SO}_4\text{H}_2, \text{SO}_4\text{H}_2, \text{SO}_4\text{H}_2 \parallel$ Copper plate.

When the metals are connected by a good conductor, such as the copper wire, the SO_4 radicle which is next to the zinc unites with it, while the H_2 unites with the SO_4 of the next molecule, and so on; the H_2 of the last molecule being liberated on the surface of the copper. Thus a molecule of zinc sulphate (Zn SO_4) is formed, and a molecule of hydrogen is liberated. Then other molecules are polarised and decomposed in like manner, and thus the action continues.

¹ The current from so small a battery is, of course, weak; but if a part of the wire is straightened and placed in a north-and-south direction, and a small compass is held as close to it as possible, a distinct deflection of the needle will be noticed; the tendency of an electric current being to set a magnet at right angles to its own direction.

It should be observed that, while the metallic connection between the two metals is maintained, the zinc alone is acted on, and not the copper, which remains bright. This illustrates the use of zinc in protecting iron from rust, as in the ordinary galvanised iron (which is iron coated with zinc). When a piece of this is exposed to air and moisture, the iron (though rapidly attacked when alone) remains unaltered so long as there is any zinc in contact with it.

✓ Preparation of a set of borax beads.

Since so many of the metals hitherto studied give characteristic colours when added to a bead of borax, it will be interesting and useful to keep a set of characteristic borax beads, as a help to the memory, and as a standard of comparison. Such a set may be conveniently made as follows:—

Seal one end of a glass tube about 6 cm. long and 2 mm. internal diameter. Place near the blowpipe a deep porcelain dish, about 10 cm. in diameter (a porcelain mortar, if glazed inside, or large tea-cup will serve the purpose), perfectly clean and dry. After making the bead in the usual way, and while it is still fluid, tap the platinum wire somewhat obliquely on the edge of the porcelain dish. The bead will detach itself and roll round the side of the dish, finally coming to rest at the bottom. It will be found to have preserved its spherical shape; and if the colour is satisfactory, it should be placed at once in the glass tube, since its surface would soon effloresce in the air. Other beads may be formed in the same way, and dropped one by one into the tube, from which they should not much differ in diameter. When the set is complete, the tube should be heated about 5 or 6 mm. above the last bead, drawn out, and sealed, thus preserving the beads from further change.

Two beads should be preserved in each case; the one showing the colour imparted by the substance in the oxidising, the other in the reducing flame.

The following list includes nearly all the substances which impart characteristic colours to borax glass:—Chromium, manganese, nickel, cobalt, iron, copper.

Group IV.

Metals which are separated from solutions by ammonium carbonate.

BARIUM, STRONTIUM, CALCIUM.

These three metals form a very well-defined natural group, showing analogies to one another quite as close as those which exist between chlorine, bromine, and iodine. Strontium seems always to occupy the middle place; and the points of resemblance and of difference between the elements should be carefully noted in examining their compounds and reactions

1. BARIUM.

[Symbol of atom, Ba.

Weight „ 137 hydrogen-atoms.]

A striking characteristic of the compounds of barium is their high density. If any minerals containing barium, such as Barite (barium sulphate) or Witherite (barium carbonate), are at hand, the density of one or more of them may be taken in the usual way and compared with the density of marble or other ordinary rock.

Compounds of Barium.

	Formula of molecule.
[Typical examples,—Barium chloride,	Ba Cl ₂
„ oxide,	Ba O
„ hydrate,	Ba H ₂ O ₂
„ dioxide,	Ba O ₂]

1. Barium hydrate.

Barium oxide (which is prepared by strongly heating barium nitrate; a process which will be illustrated under STRONTIUM) readily combines with water, just as calcium oxide has been proved to do, p. 66. The resulting barium hydrate is, however, far more soluble in water than calcium hydrate.

Place a small lump (as large as a pea) of barium oxide in a test-tube, and pour on it a few drops of water. If the barium

oxide is pure, and has not been exposed to the air, it will swell up, evolving much heat as it combines with the elements of the water to form barium hydrate¹. Pour about 8 or 10 c.c. of water upon the mass, heat it to boiling, and filter it while hot into a clean test-tube. Crystals of barium hydrate will be deposited as the liquid cools, since the salt is much more soluble in hot than in cold water (differing from calcium hydrate in this respect). Observe also the alkaline reaction of the solution on reddened litmus and turmeric paper.

This solution is often called 'baryta water,' and may be used in the laboratory for the same purposes as lime-water; for instance, as a test for carbon dioxide.

Place a little of the solution in a test-tube; dip the long branch of an elbow-tube into it, and blow gently through it for a few seconds. A white cloudiness of barium carbonate will be formed.

2. Preparation of Barium dioxide.

When barium oxide is heated, and oxygen gas passed over it, each molecule of the oxide unites with one atom of oxygen to form barium dioxide. For ordinary purposes it is most convenient to evolve the oxygen in contact with the barium oxide, in the following way:—

Place about a gramme of barium oxide in a mortar, grind it to powder, then add rather more than an equal quantity of potassium chlorate, and mix the two substances intimately with the pestle. Place the mixture in an iron spoon or a small porcelain crucible, and heat it rather strongly over a Bunsen's burner. It will at first melt and effervesce, and finally a low incandescence will spread through the mass, the barium oxide burning in presence of the chlorate (precisely in the same way as carbon or any other combustible body) with formation of barium dioxide². Allow the semi-fused mass to cool, then detach it from the spoon, grind it to fine powder, and keep it in a corked tube for use in experiments.

¹ $\text{BaO} + \text{H}_2\text{O} = \text{BaH}_2\text{O}_2$

² $3\text{BaO} + 2\text{KClO}_3 = 3\text{BaO}_2 + 2\text{KCl}$

Tests for compounds of Barium.

[A solution of barium chloride, containing 1 grm. of the salt in 25 c.c. of water, may be used.]

1. Their solutions, when tested with ammonium sulphide, give no precipitate.

To a portion of the solution add a drop of solution of ammonium sulphide. No precipitate will be formed, since barium sulphide is soluble in water, a property which distinguishes it from the sulphides of the metals included in the previous groups.

*2. With ammonium carbonate they give a white precipitate.

To another portion add a drop of solution of ammonium carbonate, and warm the liquid. A white precipitate of barium carbonate will be formed, which will readily dissolve, with evolution of carbon dioxide, on addition of a few drops of dilute hydrogen chloride.

*3. With calcium sulphate they give a white precipitate immediately, which is quite insoluble in acids.

To another portion add about one-third its volume of solution of calcium sulphate. A white precipitate of barium sulphate will be immediately formed, insoluble in hydrogen chloride.

The same reaction has already been employed to detect the presence of a sulphate (p. 289).

*4. With potassium chromate they give a yellow precipitate.

To another portion add a little solution of potassium chromate. A yellow precipitate of barium chromate will be formed, which is sometimes used as a paint, having the advantage over lead chromate of not being blackened by sulphides.

*5. Heated on platinum wire in the Bunsen's burner flame, they tinge the flame green.

Make a small loop (smaller than that intended for a borax bead, p. 100) at the end of a piece of platinum wire, dip it into strong hydrogen chloride (a few drops should be placed in a

watch-glass), and hold it just within the edge of the upper part of the flame of a Bunsen's burner (or, better, of a gas blow-pipe) until it does not itself impart any colour to the flame. Then moisten it again with hydrogen chloride, dip it into a little barium chloride, and hold it again in the flame. The barium chloride will, as it volatilises, impart to the flame a bright green colour.

From this property¹ barium salts are much used in making fireworks.

Additional Experiments.

1. Preparation of Hydrogen dioxide.

[Formula of molecule, H_2O_2 .]

This can be obtained by acting upon barium dioxide with an acid, the hydrogen of which unites with all the oxygen of the substance, while the other radicle unites with the barium.

Place about 1 grm. of powdered barium dioxide in a mortar, add a little water, and grind the whole till it forms a thin cream. Pour into the mortar about 6 or 8 c.c. of dilute hydrogen chloride, and mix it quickly with the semi-fluid mass, which ought to dissolve readily and completely; if not, a little more hydrogen chloride must be added at once. A slight effervescence will take place, owing partly to the presence of carbonate as an impurity in the barium dioxide, partly to the decomposition of the dioxide with evolution of oxygen gas. If, however, the hydrogen chloride is kept in excess, the amount of decomposition is small, and a solution is obtained containing barium chloride and hydrogen dioxide¹.

2. Properties of Hydrogen dioxide.

[The solution just made may be used, since the presence of barium chloride will not interfere with the experiments.]

This substance shows a great tendency to give up one of the atoms of oxygen which its molecule contains, thus becoming ordinary water². Hence it is a very powerful oxidising agent, and an experiment illustrating this property has been given already under CHROMIUM (p. 427). But it has scarcely less strongly marked

¹ $\text{BaO}_2 + 2\text{HCl} = \text{BaCl}_2 + \text{H}_2\text{O}_2$

Potassium chloride is, of course, also present.

² $\text{H}_2\text{O}_2 = \text{H}_2\text{O} + \text{O}$

reducing powers; the atom of oxygen which it gives up seeming to elicit a fellow-atom from other substances. Thus the two atoms from different sources combine to form a single molecule of oxygen gas¹, while both the hydrogen dioxide and the substance which it acts upon are simultaneously reduced.

A. Its oxidising powers.

(a) Make a very dilute, strongly acid solution of indigo sulphate precisely as directed in expt. 2, p. 163, and add to it a few drops of the solution of hydrogen dioxide. [A precipitate of barium sulphate will, of course, appear, owing to the barium chloride present; but this may be disregarded.] On heating the mixture to boiling, the blue colour of the indigo will disappear; the hydrogen dioxide having given up oxygen to it, just as hydrogen nitrate does, expt. 3, p. 160.

This illustrates one of the practical uses of hydrogen dioxide; *viz.* for bleaching purposes.

(b) Add a few drops of the solution of hydrogen dioxide to a dilute solution of potassium iodide (three or four drops of the laboratory solution diluted with 5 c.c. of water). Iodine will be liberated by degrees, colouring the liquid yellow, and giving the characteristic blue compound if a little solution of starch is added.

In this case hydrogen iodide (formed by the action of the excess of hydrogen chloride upon the potassium iodide) is decomposed, its hydrogen uniting with oxygen, while iodine is set free².

B. Its reducing powers.

(a) Put a little manganese dioxide into a test-tube, and pour on it some of the solution of hydrogen dioxide. A strong effervescence will take place, owing to the formation of oxygen as above explained: half of it coming from the hydrogen dioxide, and half from the manganese dioxide. The latter is reduced to protoxide, which dissolves in the hydrogen chloride present, forming manganese protochloride³.

(b) Add a little hydrogen dioxide to some rather dilute solution of potassium permanganate. The deep purple liquid will become colourless, manganese protochloride being formed, while oxygen is

¹ Other examples of the building up of a molecule of an element from two different sources have been given on pp. 243, 258, 281.

² $2 \text{HI} + \text{H}_2\text{O}_2 = 2 \text{H}_2\text{O} + \text{I}_2$

Observe the *gradual* way in which the iodine is liberated; this being one of those chemical actions which proceed at a definite measurable rate and not instantaneously.

³ $\text{MnO}_2 + \text{H}_2\text{O}_2 + 2 \text{HCl} = \text{MnCl}_2 + 2 \text{H}_2\text{O} + \text{O}_2$

evolved with effervescence¹. It is possible that this reaction may be strictly analogous to that of hydrogen dioxide on chromates, a higher and less stable manganese oxide being formed momentarily, which at once loses the greater part of its oxygen.

2. STRONTIUM.

[Symbol of atom, Sr.

Weight „ 87.5 hydrogen-atoms.]

Compounds of Strontium.

[Typical examples,—Strontium oxide,	Formula of molecule.
„ nitrate,	Sr O
„ chloride,	Sr(NO ₃) ₂
„ sulphate,	Sr Cl ₂
	Sr SO ₄]

These greatly resemble the corresponding compounds of barium, the differences between them being rather of degree than of kind. Strontium sulphate, for example, is slightly more soluble in water than barium sulphate: strontium hydrate is less soluble than barium hydrate. There is a great contrast, however, between the colours they impart to flame, respectively.

Preparation of Strontium oxide, and hydrate.

This (and also barium oxide) is best obtained by strongly heating the nitrate, when it breaks up (like lead nitrate, p. 166) into strontium oxide, nitrogen tetroxide, and oxygen².

Place about 2 grms. of crystallised strontium nitrate in an iron spoon, or on a piece of a broken evaporating dish, and heat it to full redness before the gas blowpipe. The salt will fuse and effervesce, owing to the evolution of nitrogen oxides and oxygen, and, finally, a dark gray porous mass of strontium oxide will be left. When this is cool, pour a few drops of water upon it, and notice that it 'slakes' (*i. e.* combines with the water and gets hot) like the corresponding barium and calcium oxides, and that its solution in water has an alkaline reaction on test-paper.

¹ $2 \text{KMnO}_4 + \text{H}_2\text{O}_2 + 6 \text{HCl} = 2 \text{MnCl}_2 + 2 \text{KCl} + 4 \text{H}_2\text{O} + 3 \text{O}_2$

² $2 \text{Sr}(\text{NO}_3)_2 = 2 \text{SrO} + 2 \text{N}_2\text{O}_4 + \text{O}_2$

Tests for compounds of Strontium.

[A solution of strontium nitrate, containing 1 gm. of the salt dissolved in 25 c.c. of water may be used, and the experiments should be tried in the same way as those with barium.]

1. With ammonium sulphide they give no precipitate.
- *2. With ammonium carbonate they give a white precipitate.
- *3. With calcium sulphate they give no immediate precipitate, but a white precipitate forms in four or five minutes.

This is owing to strontium sulphate being decidedly more soluble in water than barium sulphate; hence, when such a weak solution is used as that of calcium sulphate necessarily is, the precipitate only forms gradually. If dilute hydrogen sulphate (the ordinary laboratory solution) is added to the solution of strontium nitrate, a precipitate forms at once.

- *4. With potassium chromate they give no precipitate.
- *5. Heated on platinum wire, with hydrogen chloride, in the Bunsen's burner flame, they tinge the flame crimson.

If the flame is looked at through a piece of deep blue glass, it still appears of a crimson colour, while the ordinary Bunsen's burner flame is almost invisible.

3. CALCIUM.

[Symbol of atom, Ca.

Weight „ 40 hydrogen-atoms.]

Compounds of Calcium.

[Typical examples,—Calcium oxide,	Formula of molecule.
„ sulphate,	CaO
„ carbonate,	CaSO_4
• „ chloride,	CaCO_3
	CaCl_2

Several of these have been incidentally prepared and experimented on already. Thus calcium chloride was one of the

products obtained in the preparation of ammonia (p. 149), and of carbon dioxide (p. 187); calcium carbonate was formed by the action of carbon dioxide on lime-water (p. 191); and calcium sulphate was obtained when hydrogen sulphate acted upon fluorspar in the preparation of hydrogen fluoride (p. 265).

If any of the native compounds of calcium are at hand, such as Calc spar, Chalk, Marbles, Limestones, Corals (forms of calcium carbonate); and Selenite, Gypsum, Alabaster (forms of calcium sulphate), their crystalline form (if any) and other characters should be noted, and some of them at least should be examined for calcium by the tests given later on.

Formation of Calcium oxide.

This, which is the ordinary quicklime, is obtained by heating the carbonate to redness (as is done on a large scale in lime-kilns), when it breaks up into calcium oxide and carbon dioxide¹.

Place a piece of reddened litmus-paper in a porcelain dish; lay on the paper a small fragment of marble or chalk, about as large as a pea, and pour a few drops of water from a washing bottle over the marble. The colour of the litmus-paper will not be altered, since calcium carbonate is quite insoluble in water. Place the fragment of marble on a piece of platinum foil, fold a corner of the foil over it to prevent loss of heat by radiation, and heat it to full redness before a Herapath's blow-pipe for a minute or two. Place it, when cool, upon the litmus-paper, and add a drop or two of water. The paper will now turn blue, since the marble has been decomposed and calcium oxide formed, as above explained, and the latter unites with the elements of water to form calcium hydrate, which has been already shown (p. 67) to be soluble in water and to give an alkaline reaction.

Tests for compounds of Calcium.

[A solution of calcium chloride, containing 1 grm. of the salt dissolved in 50 c.c. of water may be used. The experiments should be

¹ $\text{CaCO}_3 = \text{CaO} + \text{CO}_2$

made in the same way as in the case of the barium and strontium salts.]

1. Their solutions, when tested with ammonium sulphide, give no precipitate.

*2. With ammonium carbonate they give a white precipitate.

*3. With calcium sulphate they give no precipitate, even on standing for ten minutes.

This result would be naturally expected, since no more calcium sulphate can be formed than exists already in the solution, and there is obviously more than enough water present to keep that amount dissolved.

[Calcium sulphate is, however, not very soluble in water, and nearly insoluble in alcohol. To prove this—

Add two or three drops of dilute hydrogen sulphate to some of the solution of calcium chloride, and divide the liquid into two portions.

(a) Set one portion aside for a time, shaking it occasionally. A white crystalline precipitate will gradually form.

*(b) Add to the other portion some alcohol. A white precipitate will appear at once.]

4. With potassium chromate they give no precipitate.

*5. With ammonium oxalate in neutral solutions they give a white precipitate.

This property, it will be remembered, was employed as a test for an oxalate, p. 220.

*6. Heated on platinum wire in the Bunsen's burner flame they tinge the flame orange red.

If the flame is looked at through a piece of deep blue glass, it appears greenish gray; since glowing vapours of calcium compounds give out many rays besides red and orange rays, and the blue glass absorbs the latter, but not the others.

Additional Experiments.

1. Hardness of water.

Water is said to be 'hard' when it refuses to form a lather or permanent froth with soap. This hardness is mainly due to the presence of calcium salts in the water, especially calcium-hydrogen

carbonate¹ and calcium sulphate. These decompose the soap (which is chiefly sodium oleate and margarate), forming calcium oleate, &c., which are insoluble in water.

Dissolve 1 grm. (a piece about as large as a pea) of common yellow soap in 20 c.c. of distilled water, warming² it gently.

(a) Put 100 c.c. of distilled water into a small gas bottle, add about 2 c.c. of the soap solution, and shake it up thoroughly. A thick, fairly permanent layer of froth will be produced.

(b) Put 100 c.c. of common hard water³ into a small gas bottle, add about 2 c.c. of the soap solution, and shake it up. If the water is moderately hard, it will become milky (owing to the precipitation of calcium oleate, &c.), and no permanent layer of froth will be formed; the bubbles bursting almost as soon as the shaking is discontinued. Add 2 c.c. more of the soap solution and shake it up again. If the water is very hard no lather will even now be formed, and more soap solution should be added in successive small portions, the mixture being vigorously shaken after each addition. A point will finally be reached at which enough soap has been added to decompose all the calcium salts, and then any further addition will produce a lather lasting unbroken for five minutes or more.

If we try different samples of hard water in the above way, and observe how much soap has to be added to each in order to get a permanent lather, we gain a knowledge of the comparative hardness of each sample. This is the basis of Clark's process for determining the hardness of waters.

In cases where the hardness of the water is chiefly or entirely due to the presence of calcium-hydrogen carbonate, the water may be 'softened' either (a) by boiling it (in which case the calcium compound is decomposed in the manner already illustrated, p. 191), or (b) by adding just enough calcium hydrate to form the neutral insoluble carbonate⁴ (in which case the whole of the calcium, both that originally present in the water, and that present in the calcium hydrate added, will be precipitated). This latter is the principle of Clark's process for softening water (now extensively used), and may be illustrated in the following way, if hard water of the above kind⁴ is at hand (as in chalk and limestone districts).

¹ The formation of this has been already illustrated, p. 191.

² If no hard water is at hand, add 10 c.c. of solution of calcium sulphate to 90 c.c. of rain water or distilled water, and use it for the above experiment.

³ $\text{CaH}_2(\text{CO}_3)_2 + \text{CaH}_2\text{O}_2 = 2\text{CaCO}_3 + 2\text{H}_2\text{O}$

⁴ If the hardness is due to the presence of calcium sulphate, it cannot be removed by either of the above methods.

Put 100 c.c. of the hard water into a flask, and add lime-water, little by little, with frequent shaking, until the water just shows a *slight* alkaline reaction (proving that the lime is present in slight excess). A precipitate of calcium carbonate will be formed, which should be left for two or three hours to subside. If the clear water is then poured off and tested with soap as above, a permanent lather will be produced, as with the distilled water.

2. Preparation of plaster casts.

The mineral Gypsum (native calcium sulphate) contains two molecules of water of crystallisation attached to each molecule. This water is driven off by heating the powdered mineral to a temperature of 250° , and the anhydrous calcium sulphate (the common 'plaster of Paris') thus obtained combines with a considerable quantity of water, the whole solidifying by degrees into a hard porous mass. Moreover it expands in solidifying, and hence very sharp casts of medals can be obtained.

Take a medal or large coin, and having slightly greased its surface by rubbing it with a cloth moistened with oil, roll a strip of paper (about 1 cm. broad) round its edge, so as to form a shallow circular trough; then fasten down the end of the strip by sealing-wax or by a fold or two of string. Place 20 c.c. of water in a porcelain dish, and shake into it gradually sufficient fresh plaster of Paris to form a thin paste, stirring the mixture continually with a glass rod. As soon as the whole is thoroughly mixed, pour over the coin sufficient of it to fill the trough, and stir it with a feather or splinter of wood, in order to detach any bubbles of air which may remain adhering to the surface of the coin.

[Wash out the dish containing the residue of plaster at once, or it will be difficult to remove the hardened material.]

Leave the whole at rest for several hours, in which time you will find that the paste has solidified, or 'set,' as it is termed, the calcium sulphate having (as above explained) combined chemically with the water. Unroll the paper rim, and carefully detach the coin from the plaster by gently pulling them apart. You will thus obtain a copy of the coin in plaster, but reversed, the raised parts of the coin forming depressions in the plaster. The cast should be left for several hours in a drying cupboard, or in front of a fire, in order to dry it thoroughly.

When dry, it may be used as a mould from which to obtain a facsimile of the original medal. For this purpose it should first be thoroughly saturated with wax by placing it, face upwards, in a

porcelain dish containing some melted wax or paraffin (such as a portion of a candle) and heated on a sandbath. The wax will rise by capillary action through the porous plaster, and when the upper surface appears thoroughly wet, it may be taken out and placed on a plate to cool. A paper rim should then be fastened round it, and, after slightly oiling the surface, a cast may be made in plaster as above directed. Or it may be covered with plumbago, and copper deposited on it by the electrotype process described already, p. 355.

Group V.

Metal which is separated from solutions by sodium phosphate in presence of ammonium salts.

MAGNESIUM.

[Symbol of atom, Mg.

Weight „ 24 hydrogen-atoms.]

The remarkably low density of metallic magnesium (only 1.75) should be noticed. Its pliability (much increased by moderately heating it) and its slight tenacity, in which respects it resembles zinc, can be observed in a piece of the narrow ribbon (rolled, not drawn) in which it is usually sold: this, when sharply bent double, as in creasing a sheet of paper, breaks in two. Its strong affinity for oxygen, on which its practical use for illuminating purposes and fireworks depends, has been illustrated already, pp. 124 and 192.

Compounds of Magnesium.

[Typical examples,—

Magnesium oxide,

„ sulphate,

„ -ammonium phosphate, Mg (H₄N)PO₄]

Formula of molecule.

Mg O

Mg SO₄

1. Magnesium sulphate.

Magnesium, like zinc and iron, readily acts upon most acids, displacing their hydrogen. When it acts upon hydrogen sulphate, magnesium sulphate ('Epsom salts') is formed, which

(unlike the sulphates of barium, strontium, and calcium) is very soluble in water.

Place a bit of magnesium ribbon about 15 cm. in length in a test-tube, add 5 c.c. of water, and then one or two drops of dilute hydrogen sulphate. Hydrogen gas will be evolved with effervescence, and the metal will readily dissolve¹. [No more acid must be added than is absolutely required to dissolve it.] When the action has ceased, pour off the liquid into a small porcelain dish, and evaporate it down until it begins to crystallise. Long prismatic crystals of magnesium sulphate will be deposited as the solution cools: these, after the liquid has been poured off from them, should be rinsed once with a little water, to remove adhering acid, and then redissolved in about 20 c.c. of water, and the solution reserved for experiments.

2. Magnesium oxide.

Place a piece of reddened litmus-paper in a porcelain dish, and moisten it with water. Cut off a piece of magnesium ribbon or wire about 10 cm. in length, hold it in the crucible tongs over the porcelain dish, and apply the lamp-flame to one extremity. The metal will take fire and burn with an intense white light, forming white flakes of magnesium oxide, which should be allowed to drop upon the test-paper, and spread over it with a glass rod. The blue colour of the paper will be restored, since magnesium oxide (like calcium oxide, p. 67) combines with water to form a hydrate which has an alkaline reaction and is slightly soluble in water, though much less so than calcium hydrate.

Tests for compounds of Magnesium.

[The solution of magnesium sulphate, already made (or the ordinary laboratory solution), may be used.]

A characteristic of magnesium salts is their tendency to form double salts with those of ammonium; such double salts being, as a rule, more soluble than the simple magnesium salts. Hence we can often prevent the precipitation of the latter, and

¹ $\text{H}_2\text{SO}_4 + \text{Mg} = \text{MgSO}_4 + \text{H}_2$

redissolve them when formed, by the addition of ammonium chloride.

1. Their solutions, when tested with ammonium carbonate, give no immediate precipitate.

Add eight or ten drops of solution of ammonium carbonate to some of the solution of magnesium sulphate. No precipitate will be formed until after the lapse of some time, when a slight crystalline precipitate of magnesium-ammonium carbonate will appear. The formation of this is still slower when ammonium chloride is present, and hence the metals of Group IV can be completely separated by ammonium carbonate from magnesium, if ammonium chloride has been previously added.

2. With sodium carbonate they give a white precipitate.

To another portion add some solution of sodium carbonate, and warm the mixture. A precipitate of magnesium carbonate will be formed, which will readily dissolve on addition of a few drops of solution of ammonium chloride.

***3. With sodium phosphate, in presence of ammonium salts, they give a white crystalline precipitate.**

Add to another portion of the solution five or six drops of solution of ammonium chloride, then a drop or two of solution of ammonia, and lastly a drop of solution of sodium-hydrogen phosphate. A white granular precipitate will be formed, consisting of magnesium-ammonium phosphate.

[To illustrate the delicacy of this reaction, you may place one drop of the solution of magnesium sulphate in a clean test-tube, add about 10 c. c. of water, and then successively a few drops of solution of ammonium chloride, a few drops of ammonia, and a drop of solution of sodium phosphate, and shake the mixture thoroughly. If no precipitate is produced at first, dip a clean glass rod into the solution, and gently rub the sides of the test-tube with it. Crystals will soon begin to form along the lines at which the rod touched the sides of the tube, especially if the liquid is agitated for a few seconds.]

***4. Heated on charcoal before the blowpipe they leave a white residue, which, when moistened, with cobalt nitrate and re-ignited, turns pink.**

Place a small crystal of magnesium sulphate on charcoal and heat it strongly before the blowpipe. Moisten the white infusible residue (which consists of magnesium oxide) with solution of cobalt nitrate, and heat it again. The mass, when cool, will be found to have acquired a faint pink colour.

[Compare the results obtained with zinc oxide, p. 433 (green colour); and with aluminium oxide, p. 431 (blue colour).]

Group VI.

Metals which are not separated from solutions by any of the reagents hitherto employed.

POTASSIUM, SODIUM, AMMONIUM, HYDROGEN.

1. POTASSIUM.

[Symbol of atom, K (kahum).]

Weight „ 39 hydrogen-atoms.]

Properties of Potassium.

[It must be borne in mind that potassium is a rather dangerous substance. No moisture must on any account be allowed to touch it. It must always be kept immersed in the mineral naphtha sold for the purpose. Great care should be taken that neither potassium itself nor potassium hydrate gets under the finger nails.]

1. It has a bright lustre, is soft, and becomes quickly oxidised when exposed to air.

Take a small piece of potassium, about as large as a pea, out of the bottle, free it from adhering naphtha by pressing it between folds of blotting-paper, and cut it in two with a knife. Notice the softness of the metal, the brilliant lustre of the freshly-cut surfaces, and the rapidity with which the latter are tarnished in the air, owing to the formation of a film of potassium oxide.

2. It is lighter than water, and hence floats upon it.

3. It decomposes water, liberating hydrogen.

Pour some distilled water into a plate or large porcelain dish, and wet the sides of the dish above the surface of the water by rubbing them with the moistened finger¹.

* [Place near at hand a large funnel, to hold over the potassium while burning.]

Take up one of the pieces of potassium in the crucible tongs and drop it in the centre of the dish of water. It will immediately take fire, burning with a violet flame as it floats from side to side of the dish. The water is decomposed by the metal, a portion of its hydrogen being replaced by potassium, with formation of potassium hydrate². The heat produced is sufficient to kindle the hydrogen evolved, and to volatilise a small portion of potassium, which gives the flame its violet tinge. Immediately on the cessation of the flame, you will observe the globule of potassium hydrate floating red-hot upon the water. Cover it *at once* with the inverted funnel, and observe that in a second or two it disappears with a slight explosion. The reason is this—The globule, while red-hot, was not in actual contact with the water, but was supported on a cushion of steam. As it cooled, a point arrived at which the layer of steam was condensed, and the globule touched the water, causing a fresh burst of steam sufficient to scatter portions of the globule to a considerable distance. It is well, therefore, to cover the substance with a funnel, as above directed, lest the eyes should suffer.

After burning the other piece of potassium in a similar way, you may examine the solution in the dish. It will have acquired a sharp caustic taste, and the colour of a piece of red-dened litmus-paper dipped into it will be changed to blue. If the liquid is evaporated to dryness a white residue of potassium hydrate will be left.

¹ This is done in order to prevent the globule of potassium adhering to the sides, instead of floating freely on the water. It is a good plan to rinse out the dish, just before using it, with a little solution of caustic potash, and then with clean water.

² $2 \text{H}_2\text{O} + \text{K}_2 = 2 \text{KHO} + \text{H}_2$

Compounds of Potassium.

	Formula of molecule.
[Typical examples,—Potassium hydrate,	KHO
„ carbonate,	K_2CO_3
„ nitrate,	KNO_3

1. Potassium carbonate.

This is largely manufactured from wood-ashes, and is, in fact, the substance to which the name 'potash' was originally applied. Growing plants extract the potassium compounds which all fertile soils contain; and when they are burnt, these compounds are converted into potassium carbonate (as illustrated in the case of tartrates, p. 216), which remains in the white ash and can be extracted by water.

Break up a couple of matches into small pieces (rejecting, of course, the ends coated with phosphorus), place them in a heap on wire gauze supported on a ring of the retort-stand, and set fire to them by applying the flame of a Bunsen's burner. Allow the wood to burn until only a white ash is left, then shake this into a porcelain dish and warm it with a few drops of water. The presence of an alkaline carbonate in the solution may be shown by dipping a piece of reddened litmus into it, which will be turned blue.

2. Potassium hydrate ('caustic potash').

One, and the most direct way of obtaining this substance, viz. by the action of potassium on water, has been illustrated above. It is, however, always prepared on a large scale by boiling a solution of potassium carbonate ('pearl-ash') with calcium hydrate: a process which will be explained and illustrated under the head of sodium hydrate, p. 458. The following properties of it should be examined:—

(a) It is very soluble in water, with which it combines chemically, evolving much heat.

Place a piece (about the size of an almond) of potassium hydrate in a test-tube, add 6 or 8 c.c. of water, and shake it until the whole has dissolved, which it will do very readily. Observe the great heat produced, which shows that potassium hydrate combines chemically with the water (in the same way as

sulphuric acid, p. 286). Use the solution in the following experiments, keeping the tube corked, to prevent absorption of carbon dioxide.

(b) **It deliquesces in moist air, forming a carbonate.**

It has, in fact, a very strong affinity, not only for water but also for carbon dioxide (as has been illustrated already, p. 192).

Powder a small bit of potassium hydrate, spread the powder on a watch-glass, and leave it exposed to the air for a day. It will speedily become moist, and finally deliquesce entirely into a thick liquid, as it absorbs water and carbon dioxide from the air, with formation of potassium carbonate¹.

The presence of a carbonate may be proved by pouring the liquid into a test-tube and adding 2 or 3 c.c. of dilute hydrogen chloride: an effervescence will occur², and the escaping gas may be tested with lime-water in the usual way (p. 195).

(c) **Its solution has a strong alkaline reaction.**

Potash is, in fact, the typical 'alkali' (a word meaning 'ash').

This may be proved by putting a drop of the solution on a strip of reddened litmus. The reason why the blue colour of the litmus is restored has been explained already, p. 122, note.

(d) **It combines with oils and fats, forming soap.**

Pour a little water into a test-tube and add a few drops of olive oil (common 'sweet oil') which will, of course, float on the water and not mix with or dissolve in it at all, even when shaken. Now add five or six drops of solution of potassium hydrate, and shake up the mixture. A thick cream-like solution of soap will be produced; the potassium hydrate having acted on the oleates and stearates present in the oil, to form potassium oleate and stearate, of which 'soft soap' is mainly composed.

(e) **It acts upon most organic substances, decomposing and dissolving them.**

¹ $2 \text{ KHO} + \text{CO}_2 = \text{K}_2\text{CO}_3 + \text{H}_2\text{O}$

² Potassium hydrate itself does not effervesce when an acid is added.

Put a small bit of flannel (or silk) into the remainder of the solution of potassium hydrate, and apply heat. It will be broken up and dissolved, but will be re-precipitated on addition of an excess of dilute hydrogen chloride.

This explains the action of caustic potash and of soap upon the skin, which it softens and dissolves.

We learn also that liquids containing much free potash should not be filtered through paper, although the action on cotton is not so strong as that on wool.

Tests for compounds of Potassium.

[A solution of potassium nitrate, containing 1 grm. of the salt dissolved in 30 c.c. of water may be used.]

Nearly all the salts of potassium are soluble in water, and hence no precipitates are formed with any of the group reagents hitherto used.

***1. Their solutions, when tested with platinum perchloride, give a yellow crystalline precipitate.**

Add to a portion of the solution of potassium nitrate a drop of dilute hydrogen chloride and then two drops of solution of platinum perchloride. Divide the liquid into two portions:—

(a) Set aside one portion for a few minutes, shaking it occasionally and stirring it with a glass rod. A yellow precipitate, consisting of minute octohedra of potassium-platinum chloride, will be gradually formed.

(b) Pour the remainder into a watch-glass and evaporate it to dryness on the sandbath, at a gentle heat. Mix in a test-tube equal volumes (about 5 c.c.) of water and common alcohol, and pour some of the mixture upon the residue, when the latter has cooled a little. Break up the dry crystalline crust with a glass rod, and stir the whole together: allow it to stand for a few moments, then decant the solution, pour on the residue some more of the weak alcohol, and stir together as before. A light yellow residue, consisting of potassium-platinum chloride, will remain, since the salt is insoluble in alcohol. This is the best

mode of applying the test when small quantities of potassium have to be detected.

***2. With sodium-hydrogen tartrate they give a white crystalline precipitate.**

Add to another portion a few drops of solution of sodium-hydrogen tartrate, rub the sides of the test-tube with a glass rod (p. 217), and shake the mixture. A crystalline precipitate of potassium-hydrogen tartrate will be formed, more quickly if some common alcohol is added.

***3. Heated on platinum wire in the Bunsen's burner flame they tinge the flame bluish lavender.**

Moisten a perfectly clean platinum wire with hydrogen chloride, dip it into a little powdered potassium nitrate, and hold it in the flame. The latter will be coloured lavender, and if looked at through a piece of deep blue glass will appear crimson¹.

2. SODIUM.

[Symbol of atom, Na (natrium).]

Weight „ 23 hydrogen-atoms.]

Properties of Sodium.

[The metal sodium requires quite as much caution in dealing with it as potassium; and the remarks on p. 452 apply with equal force to sodium and sodium hydrate.]

These should be examined in precisely the same way as the corresponding properties of potassium (p. 452).

1. Its metallic lustre, softness, and ready combination with oxygen, when exposed to air.

2. It is lighter than water.

3. It decomposes water, liberating hydrogen and forming sodium hydrate.

It will be found that the metal has many points of resemblance to potassium, but that it does not tarnish quite so readily in the air, and that when placed upon water it causes the evo-

¹ Glass coloured with cobalt transmits both blue and red rays, and the light emitted by ignited potassium vapour contains many of the latter.

lution of hydrogen, but that the action is not so violent as to inflame the gas.

If, however, a piece of blotting-paper is floated on the water, and a bit of sodium is placed in the centre of it so as to confine it in one place and thus prevent the distribution of the heat, the gas evolved will catch fire, and burn with an intense yellow flame, the colour being due to the volatilisation of a portion of the sodium.

[Be careful to hold the large funnel over the red-hot globule, the moment that the flame goes out.]

4. It unites with mercury, forming an amalgam.

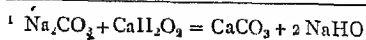
Place in a small dry test-tube a globule of mercury about twice as large as a pea. Cut off a piece of sodium about half the size, and carefully free it from naphtha by blotting-paper; then cut it into a number of small pieces (no larger than a pin's head), and, having previously heated the mercury slightly, add to it the bits of sodium, one by one. The two metals will combine with a slight explosion, forming a semi-fluid alloy or amalgam. Reserve it, corking the tube tightly, for use in a future experiment, p. 464.

Compounds of Sodium.

	Formula of molecule.
[Typical examples,—Sodium hydrate,	(Na HO)
„ chloride,	(Na Cl)
„ sulphate,	Na ₂ SO ₄
„ carbonate,	Na ₂ CO ₃
„ -hydrogen carbonate,	NaHCO ₃
Many other sodium salts have been made and examined already ; e.g. sodium phosphate, p. 300.]	

Preparation of Sodium hydrate ('caustic soda').

This is made by boiling a rather dilute solution of sodium carbonate with an excess of lime: sodium carbonate and calcium hydrate giving sodium hydrate and calcium carbonate, which latter is precipitated¹.



Powder about 3 or 4 grms. of quicklime, and mix it in the mortar with 10 c.c. of water. Place 25 c.c. of solution of sodium carbonate (the ordinary laboratory solution) in a beaker, add to it, the whole of the lime and boil it for ten minutes, covering the beaker loosely with a watch-glass or glass plate, to prevent access of carbon dioxide from the air. Allow the precipitate of calcium carbonate to subside for a minute, then pour off a few drops of the clear solution into a test-tube, and add excess of dilute hydrogen chloride. No effervescence should occur, thus proving that all the carbonate has been decomposed.

[If there is any effervescence a little more lime must be ground up with water and added to the remainder of the liquid in the beaker, and the boiling continued for a few minutes longer.]

When you have thus ascertained that the reaction is complete, the contents of the beaker may be filtered into a test-tube (the solution of sodium hydrate is not so concentrated as to destroy the filter), and used in the next expt.

[Potassium hydrate is prepared in exactly the same way, a solution of potassium carbonate (1 part by weight of the salt dissolved in not less than 12 parts of water¹) being substituted for the sodium carbonate.]

The properties of sodium hydrate closely resemble those of potassium hydrate, and need not be fully examined. Its chief use is for the manufacture of ordinary soap, which may be illustrated as follows:—

Put about 10 c.c. of the solution of sodium hydrate into an evaporating dish, add about 2 c.c. (rather less than a teaspoonful) of olive oil, and boil the mixture with frequent stirring until a clear viscid solution is obtained. Add to this 2 or 3 grms. of common salt, stir, and boil again for a minute: then allow it to cool. White, curdy flakes of common 'hard soap' (sodium oleate, stearate, &c.) will be separated (since soap is insoluble in solution of sodium chloride) and rise to the top: while the solution below contains glycerin.

¹ If the solution is stronger than this, the whole of the carbonate cannot be decomposed by the calcium hydrate.

Sodium-hydrogen carbonate ('bicarbonate of soda').

Ordinary sodium carbonate ('washing soda') is made from common salt by processes which cannot well be illustrated on a small scale. It combines readily, in presence of water, with carbon dioxide, forming sodium-hydrogen carbonate, which is much less soluble in water than the normal salt.

Dissolve 5 grms. of ordinary crystallised sodium carbonate in 10 c.c. of water, by the aid of heat. While the solution is cooling, fill a large gas-bottle with carbon dioxide by displacement, in the manner shown in fig. 81, p. 188 (a few small lumps of marble or chalk in a large test-tube, fitted with funnel and elbow-tubes, will give enough gas). When the solution of sodium carbonate is quite cold, filter it from any deposited crystals, pour it into the gas-bottle, and shake it up in the gas, putting a small strip of the thinnest paper between the stopper and neck of the bottle; then leave it for several hours at least, occasionally shaking it. The carbon dioxide will be gradually absorbed by the salt, and crystals of sodium-hydrogen carbonate will form in the bottle¹. Collect these on a filter, and wash them with two or three changes of water; then transfer some of them to a test-tube, for use in the next expt., and dry the rest on the filter at a gentle heat.

The following properties of the salt may be observed:—

1. It is not very soluble in water, and its solution, when tested with mercury perchloride, gives scarcely any precipitate.

Shake up the crystals in the test-tube with about 5 c.c. of water. They will only gradually dissolve, differing greatly in this respect from the ordinary carbonate. Add to the solution a drop or two of solution of mercury perchloride: a slight cloudiness only will be formed, consisting of mercury oxy-chloride.

For the sake of comparison, shake up about the same quantity of the ordinary crystallised sodium carbonate with 5 c.c. of

¹ $\text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2 = 2\text{NaHCO}_3$
Compare the formation of calcium-hydrogen carbonate, p. 191.

water, noting the ready solubility of the substance, and test the solution with mercury perchloride. A dull reddish precipitate of mercury carbonate will be formed.

2. When heated to redness, it is decomposed, giving off carbon dioxide and water, and being converted into the normal sodium carbonate.

Put the dried crystals of sodium-hydrogen carbonate into a small test-tube, and heat them rather strongly. Carbon dioxide will be given off, and may be tested for in the usual way, with a pipette dipped in lime-water. When the residue in the tube is cool, dissolve it in water, and test the solution with mercury perchloride. A reddish precipitate will show that the normal carbonate is now present.

This decomposition of sodium-hydrogen carbonate by heat, with evolution of carbon dioxide, explains its use in baking to render the bread, &c., light and porous owing to the innumerable bubbles formed in the soft dough by the escaping gas.

The salt is also extensively used in making effervescing draughts; since, when acted on by acids such as tartaric acid, it gives off much more carbon dioxide than an equal weight of the normal carbonate (as will be evident on comparing the weights of the molecules of the two substances).

Tests for compounds of Sodium.

[A solution of sodium chloride, containing 1 grm. of the salt dissolved in 25 c.c. of water, may be used.]

1. Their solutions, when tested with platinum perchloride, give no precipitate.

Put a few drops of the solution of sodium chloride into a watch-glass, add a couple of drops of platinum perchloride and evaporate to dryness. A residue, but no yellow particles, will be obtained, which will completely dissolve in dilute alcohol. (Compare the result obtained in the case of potassium, p. 456.)

2. With sodium-hydrogen tartrate they give no precipitate.

In fact, all the compounds of sodium (except sodium met-

antimonate) are soluble in water, and their presence is usually inferred from the following characteristic reaction.

*3. Heated on platinum wire in the Bunsen's burner flame, they tinge the flame intensely yellow.

This has been already observed, p. 100, but should be tried again. When a piece of deep blue glass is held in front of the flame the intense yellow light is entirely cut off, and hardly anything but the faint bluish flame of the burner is visible through the glass.

Additional Experiments.

[It will be best to do these at night, or in a darkened room.]

The light emitted by ignited sodium vapour consists almost entirely of yellow rays of one definite refrangibility; and it may be interesting to examine the character of this simple 'homogeneous' light a little more closely.

1. If the rays fall on any surface which cannot reflect that particular kind of light, that surface appears perfectly black, whatever its colour may be in ordinary white light.

Melt a little sodium carbonate in the ring at the end of a piece of platinum wire, and grasp the wire in the Bunsen's holder, so that it may be held steadily just within the border of the Bunsen flame. The sodium carbonate (which is preferable to sodium chloride as being less volatile) will yield an intense yellow light for a considerable time. Place a blue flower, such as a lobelia or larkspur, or a few crystals of copper sulphate, on a sheet of white paper and hold them near the light. They will appear quite black, for the reason above explained; while if the air-holes of the burner are temporarily closed so as to get the usual luminous gas-flame, their blue colour is plainly seen.

2. If the rays fall on a surface which can reflect them, and then only (*i. e.* what we call a 'yellow' surface), that surface appears undistinguishable in colour from a white surface placed near; since although the white surface could reflect other rays, there are in the sodium light no others to fall upon it.

(a) Place a piece of strongly yellow turmeric-paper or a few crystals of potassium chromate on a sheet of white paper, and hold it in the yellow light, all other light being excluded. The yellow substances will appear of the same colour as the paper; yellow rays

only are falling upon both, and hence both appear yellow. On obtaining, however, a white flame by stopping the air-holes of the burner, the paper reflects all the white light which falls on it, while the turmeric and the potassium chromate reflect only the yellow.

(b) Form a scarlet stripe or pattern upon a sheet of white paper with mercury iodide¹. When it is held in the yellow light it will almost disappear. The reason is that mercury iodide reflects a large number of yellow rays as well as red; there are none of the latter in the sodium light, hence the substance can only appear yellow, and the paper also. A scarlet geranium shows a similar effect, and if several stripes of different brilliant colours are painted on paper they all appear of different shades of yellow or black, according to the amount of yellow rays which they can reflect.

3. AMMONIUM.

[Formula of radicle, H_4N .

Weight „ 18 hydrogen-atoms.]

The mode of preparation and properties of ammonia have been given already, p. 146; and it has been noticed that it combines directly with hydrogen salts to form substances which all agree in containing a radicle composed of 4 atoms of hydrogen united with 1 atom of nitrogen, which is called AMMONIUM. Some of these compounds are mentioned in the following list, and the preparation of nearly all of them has been already illustrated in the experiments to which a reference is given.

Compounds of Ammonium.

	Formula of molecule.
[Ammonium hydrate,	$(H_4N)HO$ (p. 152).
„ chloride,	$(H_4N)Cl$ (p. 238).
„ nitrate,	$(H_4N)NO_3$ (p. 160).
„ carbonate,	$(H_4N)_2CO_3$ (p. 89).
„ sulphide,	$(H_4N)_2S$]

The radicle, AMMONIUM, although it can be transferred from one compound to another (see, for instance, the experiment

¹ This has been already prepared, pp. 84, 92. It should be mixed with a little gum and applied with a camel's hair brush or a tuft of cotton wool.

given on p. 85), has never with certainty been isolated, owing to the extreme readiness with which it breaks up into ammonia and hydrogen. But the salts containing it so closely resemble those of potassium and sodium that it is at least possible that, if it is ever isolated, it may appear as a metal. The following experiment is thought to show that it even resembles a metal in forming an amalgam with mercury.

Preparation of Ammonium-amalgam.

This is most readily formed by acting upon ammonium chloride with sodium-amalgam; a double decomposition taking place which results in the ammonium being transferred to the mercury¹.

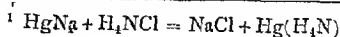
Make a strong solution of ammonium chloride by shaking up 7 grms. of the powdered salt in 20 c.c. of water, noticing the cold produced by the solution of the salt. Support the test-tube containing the sodium amalgam (already made, p. 458) in a beaker standing on a plate, and pour into it the solution of ammonium chloride. The amalgam will immediately begin to increase in bulk, swelling into a gray porous mass which will probably half fill the tube. Shake it out upon a dish; notice its pasty consistence, and also that when no longer immersed in the solution of ammonium chloride it begins to decompose, shrinking in bulk, giving off ammonia and hydrogen, and finally leaving nothing but a globule of mercury. The presence of ammonia will be proved by its smell and its alkaline action upon a piece of reddened litmus-paper held just over the decomposing mass.

Tests for compounds of Ammonium.

[The ordinary laboratory solution of ammonium chloride may be used.]

*1. They volatilise when heated, usually without decomposition.

Put a small bit of ammonium carbonate into a test-tube and



heat it rather strongly. Observe that as it becomes hot it rolls about the test-tube when shaken, without apparent friction; owing to the formation of a layer of vapour which prevents it from actually touching the glass. It will volatilise entirely, without previous fusion.

The volatility of ammonium chloride has been proved already, p. 239.

It has also been shown, in preparing nitrogen monoxide, p. 178, that ammonium nitrate is decomposed when heated and does not volatilise unchanged, thus forming an exception to the general rule.

***2. Heated with quicklime they give off ammonia.**

Place a little powdered calcium oxide in a small beaker, add just enough water to cover it, and then one or two drops of solution of ammonium chloride. Cover the mouth of the beaker with a watch-glass, on the convex (and lowermost) side of which has been spread a moist slip of reddened litmus-paper and a similar slip of turmeric-paper. Heat the beaker very gently on the sand-bath. In a short time ammonia will be evolved by the action of the calcium hydrate on the ammonium salt, and will restore the blue colour to the litmus-paper and redden the turmeric-paper. When this is seen to be the case, remove the watch-glass, notice the odour of ammonia in the beaker, and also test for it by dipping into the beaker (without touching the sides) a glass rod moistened with strong hydrogen chloride or, better (since hydrogen chloride itself fumes perceptibly), strong hydrogen acetate.

3. With platinum perchloride they give a yellow crystalline precipitate.

This has been noticed already, under PLATINUM, p. 393. The precipitate closely resembles that formed by potassium salts under similar circumstances, and hence potassium must be proved to be absent before the test can be applied to detect ammonium.

Additional Experiments.

Formation of other radicles derived from Ammonium.

Each of the four atoms of hydrogen in the molecule of ammonium can be replaced by an equivalent amount of some other radicle, and thus a large number of new radicles are obtainable. The formation of one of these, cuprammonium, has been noticed already, p. 354, and several similar radicles can be formed by the action of mercury salts.

1. Dimercurammonium chloride (Hg_2NCl).

Put some solution of ammonium hydrate into a test-tube and add a few drops of solution of mercury perchloride. A white precipitate will be formed, which is a compound of chlorine with dimercurammonium, a radicle derived from ammonium by the replacement of two atoms of hydrogen by one atom of (divalent) mercury, as the formula shows¹.

2. Tetramercurammonium iodide (Hg_2NI).

(Nessler's test for ammonium.)

This substance is formed when mercury iodide acts upon ammonium salts in presence of an excess of potassium hydrate, and its formation affords an extremely delicate test for the presence of ammonium.

In the first place a solution of mercury iodide in potassium iodide must be prepared.

Take 5 c.c. of solution of potassium iodide (the ordinary laboratory solution), and add to it, drop by drop, solution of mercury perchloride, shaking after each addition. The precipitate of mercury iodide will at first be readily redissolved. Continue the addition of mercury perchloride until the last drop produces a slight permanent precipitate, insoluble even on being shaken: then add an equal volume of solution of potassium hydrate (the ordinary laboratory solution) and filter². The solution thus made is called 'Nessler's test solution,' from the chemist who discovered it, and the following experiments will illustrate its application.

¹ The mercury oxide which would naturally be formed (in the same way as by the action of potassium hydrate, expt. b, p. 338) acts upon the ammonium radicle. Two atoms of hydrogen are taken out, and combine with oxygen, forming water; while an atom of mercury takes their place. Thus, —
 $2(\text{H}_4\text{N})\text{HO} + \text{HgCl}_2 = \text{HgH}_2\text{NCl} + \text{H}_4\text{NCl} + 2\text{H}_2\text{O}$

² The excess of potassium hydrate is not enough to act materially upon the filter.

(a) Dilute two or three drops of solution of ammonium chloride with 10 c.c. of water and add some of the Nessler's solution just made. A reddish precipitate will be formed, consisting of tetramercurammonium iodide¹; the radicle being formed by the replacement of all the four atoms of hydrogen in a molecule of ammonium by two atoms of (divalent) mercury.

(b) To show the delicacy of the test, put one drop of solution of ammonium chloride into a large test-tube and add 50 c.c. of water. Pour away the whole of this solution, and add 50 c.c. of water to the small portion still adhering to the tube. If the tube be placed on a sheet of white paper, and a few drops of Nessler's solution added, a distinct yellow colour will appear, though mere traces only of ammonium chloride can be present.

(c) Test about 50 c.c. of common rain water with Nessler's solution. It will almost invariably become yellow or orange, owing to the ammonium salts which the rain dissolves in falling through the air.

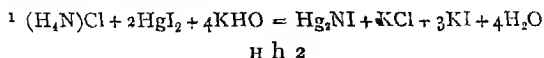
4. HYDROGEN.

[Symbol of atom, H.

The hydrogen-atom is taken as the unit of atomic weight.]

The preparation and properties of hydrogen have been already given in Sect. II. Ex. 2 (p. 124). The element, although it does not (even when liquefied and solidified) show many of the usual characters of a metal, such as bright lustre, high density, tenacity, &c., yet appears in its chemical characters to be one of the most typical members of the metallic group. It combines with all the non-metallic radicles such as chlorine, oxygen, sulphur, the phosphate radicle, &c., to form true salts, *viz.* the substances which still retain their old name of 'acids.' Moreover, when its compounds are decomposed by electricity, it always appears at the negative electrode, showing its electro-positive character.

Many of the salts of hydrogen, or 'acids,' have been prepared already: for instance:—



	Formula of molecule.
Hydrogen nitrate,	HNO_3 (p. 156)
„ chloride,	HCl (p. 236)
„ sulphate,	H_2SO_4 (p. 284)
„ phosphate,	H_3PO_4 (p. 299)
„ borate,	H_3BO_3 (p. 304).

Properties of Hydrogen salts.

The following general characteristics of acids should be noted:—

1. They, as a rule, redden blue litmus-paper, but do not alter the colour of turmeric-paper.

[The reason of the change in colour of litmus-paper has been explained on p. 122, note.]

This property has been frequently observed already (see, for instance, pp. 160, 237, 286) and it belongs to most of the hydrogen salts which are likely to be met with in the course of elementary work. Hydrogen borate, however, while it has the usual acid reaction on blue litmus-paper, turns turmeric-paper pinkish red (p. 305).

*2. They decompose sodium carbonate and other carbonates, with evolution of carbon dioxide.

This has been illustrated already, p. 195.

3. They are, in many cases, decomposed by metals such as zinc, with evolution of hydrogen gas, and formation of a neutral salt.

The action of hydrogen chloride, for instance, on zinc has been examined already, p. 80.

The presence of hydrogen salts will be easily recognised in the course of an analysis by tests 1 and 2. But it must be remembered that many double salts containing another radicle as well as hydrogen are known (for example, sodium-hydrogen tartrate), and hence another metal should always be examined for, unless the substance has the characteristic properties, such as volatility, of the hydrogen salt of the non-metallic radicle which has been detected.

PART II.

QUALITATIVE ANALYSIS OF SINGLE SUBSTANCES.

SECTION I.

EXPLANATION OF THE ANALYTICAL COURSE.

EVERY portion of matter, considered chemically, is either a single substance or an aggregate of two or more single substances. By a single substance, we mean a substance from which no part, having different properties from the rest, can be separated by any physical means, such as pounding and sifting, or the action of solvents, or distillation, or diffusion. Water, and salt, and hydrogen, and indeed most of the various substances whose properties you have been studying, are single substances¹. Other portions of matter, consisting of two or more single substances aggregated together, such as a mixture of salts, or a piece of rock, or any part of a plant or of an animal, are called mixtures.

According to this twofold division of natural objects, analysis is divided into the analysis of single substances, and the analysis of mixtures. Further, the analysis may in each case be either qualitative or quantitative, the former having for its object the identification of a single substance or of the ingredients of a mixture, the latter enquiring in what proportions the elements of a single substance, or the various single substances in a mixture, coexist.

Of the four divisions of analysis thus indicated, the present

¹ The term 'chemical substance' is often used in this sense, but has the disadvantage of suggesting a peculiar class of substances instead of expressing the simple fact.

volume treats only of the first—the qualitative analysis of a single substance.

Two further limitations should be named in order exactly to define the scope of the analytical course which follows. First, you will have observed that the preceding exercises deal only with the commoner or more abundant elements. About half the elements at present known are so rare that it is found expedient to exclude them from consideration in framing the analytical course. Secondly, of the compound radicles formed from these elements some are continually met with among natural or artificial products, while others occur but seldom. Here, again, it has been necessary to make an arbitrary limitation, and to select from a host of such radicles those of a few of the commonest substances. The problem, then, which the following analytical course supplies the means of solving should be stated thus :—Given a single substance consisting of one or more of the radicles already treated of, to find out what it is.

The great majority of the substances which present themselves for analysis consist of a combination of a simple radicle, belonging to the class of metals, with a simple or compound radicle belonging wholly or chiefly to the non-metallic class; a few contain more than one radicle of either class. For example, the molecule of sodium chloride, NaCl , consists of the simple metallic radicle Na and the simple non-metallic radicle Cl ; silver nitrate, AgNO_3 , of the simple metallic radicle Ag , and the compound non-metallic radicle NO_3 ; sodium-potassium tartrate $\text{KNa}(\text{C}_4\text{H}_4\text{O}_6)$, sodium-ammonium-hydrogen phosphate $\text{Na}(\text{H}_4\text{N})\text{H}(\text{PO}_4)$, magnesium phosphate and fluoride $\text{Mg}_2\text{PO}_4\text{F}$, exemplify the union of more than two radicles. Conformably with this fact as to the constitution of substances, the course of analysis consists of two principal parts, the one determining the metallic radicle or radicles, the other the non-metallic radicle or radicles of which a substance is formed.

It is by no means necessary actually to obtain the simplest forms of matter (the so-called ‘elements’) from a substance in order to ascertain its composition. It is sufficient to cause the formation of compounds which, from their colour, solubility, &c.,

and the conditions under which they are formed, may be recognised as substances containing particular elements. For instance, it was observed (p. 274) that when antimony sulphide (a compound of antimony with sulphur) is acted upon by an acid such as hydrogen chloride, a gas is evolved which blackens paper moistened with a solution of lead acetate. The formation of this black compound of lead, under the circumstances there given, is accepted as a proof of the presence of sulphur in the substance.

In many cases a group of two or more elements appears to be more easily detached from a substance than the individual elements; the substance, like a crystal, cleaving more easily in some directions than in others. An illustration of this will be found on p. 187. The substance, marble, from which we have considerable difficulty in obtaining carbon, oxygen, and calcium individually, we found to yield by very simple treatment a gas, the properties of which were examined. Having once ascertained that this gas is composed of carbon and oxygen in certain proportions, we are satisfied, in the examination of other substances, if we can obtain the same gas from them by the action of hydrogen chloride. Substances which yield the gas when thus treated, we place under one head and call them 'CARBONATES.' Similarly, in examining marble for its other constituent, calcium, we do not attempt to isolate the element; we stop short of this point, and are satisfied with obtaining a compound with well-marked properties, from which it has once for all been proved possible to obtain calcium. Substances from which we can obtain this compound, we class together as 'CALCIUM SALTS.'

We find, in fact, that certain groups of elements can be transferred from one compound to another, and the analysis of a substance is effected when it has been resolved into groups, the composition of which is known.

The acquaintance which has been gained in Part I with the properties of the various radicles and their compounds furnishes a means of distinguishing any one from the rest and identifying it. But it remains to be seen in what manner this end can be most

surely and quickly accomplished. It might be possible by trying in any order a sufficient number of the experiments described in the section upon the substance under examination, to discover at last its true nature; but much time would be lost upon experiments which yielded no information, the presence of other radicles might interfere with the tests for any particular one, and the analysis would not unfrequently end in inextricable confusion. We ought to start, then, with a clear perception of the relative value of the tests we are going to employ: we must select them on definite principles, and observe a definite order in applying them.

No better course can be followed in an analysis than the strictly logical one of

- 1st. Finding out the genus to which the radicle belongs.
- 2ndly. Ascertaining the species.
- 3rdly. Identifying the individual.

In this way we are enabled to concentrate our search on fewer and fewer subjects, dismissing altogether the other radicles from our attention, until finally we are led to the conviction that one particular radicle must be present.

DISTRIBUTION OF THE RADICLES INTO GROUPS FOR THE PURPOSES OF ANALYSIS.

In following out the above principle, the first step will be to take a number of solutions each containing one of the radicles under consideration, and to try the effect of some one particular test upon each. We should find that in some cases the radicle was separated by precipitation owing to the formation of an insoluble compound of it, while in the rest no apparent effect was produced. We should place all those radicles which could be separated thus, in a group by themselves. We should then try the effect of another test on each of the remaining solutions, and those radicles which could be separated by means of it would constitute another group. Proceeding thus, we could sort all the radicles into different groups, which we might dis-

tinguish by the name of the test by which all the members of the group could be separated.

The process thus indicated has been gone through with great care by chemists, and the following experiments may be made to illustrate it.

A. Non-metallic Radicles.

Place five test-tubes in the stand, and put into them, respectively, eight or ten drops of solutions of

1.	2.	3.	4.	5.
SODIUM CARBONATE.	AMMONIUM OXALATE.	AMMONIUM CHLORIDE.	POTASSIUM IODIDE.	POTASSIUM NITRATE.

[The ordinary laboratory solutions may be used¹.]

Add to each about 20 c.c. of water, and write the contents of each tube upon the strip of slate in front of it (or place a label on the tube itself).

1. Barium Chloride Test.

Pour about 5 c.c. of the solution of sodium carbonate into another tube and add a few drops of solution of **barium chloride**. A white precipitate will be formed, and if the barium chloride was added in excess the whole of the carbonate radicle might be separated as insoluble barium carbonate.

Test portions of each of the other solutions in a similar way. It will be found that barium chloride produces a precipitate in the solutions of sodium carbonate and ammonium oxalate, but not in the solutions of ammonium chloride, potassium iodide, or potassium nitrate. And by examining solutions containing other non-metallic radicles in the same way, it would be found that they could be divided into two groups, *viz.*—

Radicles which are separated from neutral solutions by barium chloride.	Radicles which are not separated from neutral solutions by barium chloride.
---	---

[See the Table on p. 479.]

¹ These salts are so selected that the presence of the other radicle (sodium, ammonium, &c.) has no influence on the formation of a precipitate.

The practical inference, then, is,—If on testing a neutral solution (containing an unknown single salt of an alkali-metal) with barium chloride, a precipitate occurs, one of the radicles in Group I must be present.

2. Silver Nitrate Test.

We next proceed to see whether, out of all the remaining radicles, some may be separated from the rest on a similar principle.

Take fresh portions of the solutions of ammonium chloride, potassium iodide, and potassium nitrate, and test each with a few drops of solution of silver nitrate. Precipitates consisting of insoluble compounds of silver will be obtained in the case of the chloride and iodide, but none in the solution containing the nitrate.

In this way we may divide all the radicles which are not precipitated by barium chloride into two groups, *viz.*—

Radicles which are separated from neutral solutions by silver nitrate.	Radicles which are not separated from neutral solutions by silver nitrate.
--	--

[See the Table on p. 479.]

Hence, by applying only two tests we are enabled, in the further course of analysis, to limit our search to the members of that group to which the radicle has thus been proved to belong.

Formation of sub-groups.

The next step will be to try the action of other reagents on the members of each group, in order to be able to carry the principle of division still further, and to arrange them in smaller sub-groups. For instance,—

Take the portions of the solution of ammonium chloride and potassium iodide which contain the precipitates produced by the addition of silver nitrate, add to each some solution of ammonium hydrate, and shake the mixture. The precipitate produced in the solution of the chloride will be dissolved, while

that which was produced in the solution of the iodide will remain undissolved. And if the same experiment was repeated with all the members of Group II, it would be found that they may be arranged in two divisions.

A.	B.
Radicles, the silver compounds of which are soluble in ammonia.	Radicles, the silver compounds of which are insoluble in ammonia.
CYANIDES.	IODIDES.
CHLORIDES.	SULPHIDES.
BROMIDES (with difficulty).	
THIOSULPHATES.	
HYPOPHOSPHITES.	
ACETATES.	

Characteristic and Confirmatory Tests.

Finally, when we have thus divided the radicles into conveniently small groups, we proceed to apply tests which give characteristic reactions with the individual members of each group. For instance,—

Take a fresh portion of the solution of potassium iodide, add a few drops of **carbon disulphide**, and one drop of **solution of chlorine**. The solution will become yellow, and after agitation the carbon disulphide will collect at the bottom of the tube in a globule of a violet colour. This, as we have already seen (p. 259), is a reaction which distinguishes an iodide from all other substances, a bromide being the only one which gives a result at all similar. We might here rest content with having obtained one reaction which is characteristic of the presence of one particular substance. But it is highly expedient to accumulate evidence, so as to leave no possible room for doubt as to the constitution of the substance under examination; and other confirmatory tests should always be tried.

Thus, in the case of the solution of potassium iodide, a precipitate has been obtained with silver nitrate, proving that the radicle belongs to Group II: this precipitate is insoluble in ammonia, and the radicle therefore is included in division B; the yellow colour of the precipitate and reaction with solution of chlorine and carbon disulphide indicate the presence of an iodide. Assuming, then, that an iodide is present, we try the

action of other tests which are known to give characteristic reactions with an iodide. For example,—

Take a fresh portion of the solution of potassium iodide, add to it a few drops of solution of starch, and then a drop of solution of chlorine. The solution will acquire an intense blue colour. This reaction is absolutely characteristic of an iodide (p. 255), and confirms the previous results.

B. The Metallic Radicles.

These may be divided into six very definite and easily distinguishable groups, in the manner illustrated by the following experiments.

Place in test-tubes about 1 c.c. of each of the following solutions (the ordinary laboratory solutions may be used), and dilute with 20 c.c. of water. Write the contents of each on the slate strip in front of the test-tube stand (or place a label on the tube itself).

1. SILVER NITRATE.	2. COPPER SULPHATE.	3. IRON PROTOSULPHATE.	4. BARIUM CHLORIDE.
	5. MAGNESIUM SULPHATE.	6. AMMONIUM CHLORIDE.	

1. Hydrogen Chloride Test.

Test portions (about 5 c.c.) of each of the above solutions with a few drops of dilute hydrogen chloride. A white precipitate will be formed in the solution of silver nitrate, but not in any of the others.

We place, then, in one group metals such as silver, which are precipitated from solutions by hydrogen chloride.

[See the Table on p. 480.]

2. Hydrogen Sulphide Test.

Take the portions of each of the solutions to which hydrogen chloride was added in the last experiment without producing a precipitate, and test each with some solution of hydrogen

sulphide. A precipitate will be produced in the solution of the copper salt, but not in any of the others.

We associate in another group metals such as copper, which are precipitated from solutions containing hydrogen chloride by hydrogen sulphide.

3. Ammonium Sulphide Test.

Take fresh portions of the solutions of iron protosulphate, barium chloride, magnesium sulphate, and ammonium chloride, and test each with solution of ammonium sulphide. A precipitate will be produced in the solution of the iron salt, but not in any of the others.

We form, therefore, into a third group metals, such as iron, which are not precipitated from solutions containing free acid by hydrogen sulphide, but are precipitated from neutral solutions by ammonium sulphide.

4. Ammonium Carbonate Test.

Take the portions of the three solutions (barium chloride, magnesium sulphate, and ammonium chloride) to which ammonium sulphide was added in the last experiment without producing a precipitate, and test each with solution of ammonium carbonate. A precipitate will be produced in the solution of barium chloride, but not in either of the others.

We constitute, therefore, another group of those metals, such as barium, which are not precipitated from their solutions by either hydrogen sulphide or ammonium sulphide, but which are precipitated by ammonium carbonate from solutions containing ammonium salts.

5. Sodium Phosphate Test.

Take the solutions of magnesium sulphate and ammonium chloride used in the previous experiments (and which therefore contain ammonium sulphide and carbonate) and test each with solution of sodium-hydrogen phosphate. A precipitate will be formed in the solution of magnesium sulphate, but not in the solution of ammonium chloride.

We place, then, in a group metals, of which magnesium is the only known example, which are not precipitated from solutions by hydrogen sulphide, ammonium sulphide, or ammonium carbonate (if the solutions already contain ammonium salts), but which are precipitated by sodium phosphate from solutions containing ammonium salts.

The sixth and last group consists of those metallic radicles, such as ammonium, which are not precipitated from solutions by any of the reagents above mentioned, and which remain as a residue, in the course of an analysis, when all the other substances have been removed from the solution under examination.

By repeating the above experiments with each of the metallic radicles treated of in Part I. Sect. III, we should be enabled to place it in some one of the above six groups, and we might construct a Table similar to that which is given on p. 480.

Summary.

The general course, then, to be pursued in a qualitative analysis of an unknown substance for one radicle, is—

Firstly, to ascertain the group to which the radicle belongs.

Secondly, to ascertain the subdivision of the group to which it belongs.

Thirdly, to ascertain which member of the subdivision is present.

Lastly, to confirm the results, by applying tests which give characteristic reactions with the radicle, the presence of which has been indicated.

In practice it is found advisable to examine a substance first for the metallic radicle it contains, chiefly for the reason that there are more cases in which ignorance of the metal present would interfere with the examination for the non-metallic radicle, than *vice versa*.

TABLE

SHOWING THE DISTRIBUTION OF THE MORE IMPORTANT
NON-METALLIC RADICLES INTO GROUPS FOR THE
PURPOSES OF ANALYSIS.

These Radicles are divided into		
I. Those which are separated from neutral solutions by Barium Chloride.		Those which are not separated from neutral solutions by Barium Chloride.
CARBONATE TARTRATE (partially) OXALATE FLUORIDE (partially) FLUOSILICATE SULPHITE SULPHATE PHOSPHATE BORATE (partially) SILICATE CHROMATE ¹ .		
II. Those which are separated from neutral solutions by Silver Nitrate.		III. Those which are not separated from neutral solutions by Silver Nitrate.
CYANIDE CHLORIDE BROMIDE IODIDE SULPHIDE THIOSULPHATE HYPOPHOSPHITE ACETATE (partially).		NITRATE CHLORATE.

¹ This is described under CHROMIUM.

SHOWING THE DISTRIBUTION OF THE MORE IMPORTANT METALS INTO GROUPS FOR THE PURPOSES OF ANALYSIS.

These Metals are divided into	
I. Metals which are separated from solutions by Hydrogen Chloride.	Metals which are not separated from solutions by Hydrogen Chloride.
SILVER MERCURY (monovalent) LEAD (partially).	
II. Metals which are separated from solutions containing hydrogen chloride by Hydrogen Sulphide.	Metals which are not separated from solutions containing hydrogen chloride by Hydrogen Sulphide.
LEAD MERCURY (divalent) COPPER CADMIUM BISMUTH ARSENIC ANTIMONY TIN GOLD PLATINUM	form sulphides which are soluble in ammonium sulphide.
III. Metals which are separated from solutions by Ammonium Sulphide.	Metals which are not separated from solutions by Ammonium Sulphide.
ZINC MANGANESE COBALT NICKEL IRON CHROMIUM ALUMINIUM.	
IV. Metals which are separated from solutions by Ammonium Carbonate.	Metals which are not separated from solutions by Ammonium Carbonate.
BARIUM STRONTIUM CALCIUM.	
V. Metal which is separated from solutions by Sodium Phosphate.	VI. Metals which are not separated from solutions by Sodium Phosphate.
MAGNESIUM.	POTASSIUM SODIUM AMMONIUM HYDROGEN.

GENERAL RULES TO BE OBSERVED IN MAKING AN ANALYSIS OF AN UNKNOWN SUBSTANCE.

1. Write out a full account of all that is done; the conditions of each experiment, the results obtained, the inferences drawn from these results.

This should be done, not more for the sake of the teacher or examiner than for the advantage of the student himself. The former has, in general, no way of ascertaining what has been done except from the contents of the note-book; the latter will find no means of gaining accuracy of thought, clearness of expression, and insight into analytical methods, more effectual than constant practice in writing out accounts of work done.

Excellent models for such descriptions may be found in the original papers on substances either newly discovered or examined for the first time, contributed by our best chemists to scientific magazines. The object of every such paper is to make clear to others the views of the author on the nature of the substance he has examined, and his reasons for adopting these views; to give the experiments which have been tried, and the inferences drawn from them. This is no less the object of the student commencing analysis. Every substance presents to him an original problem, which should be approached in the same spirit, and worked out with the same care as the most elaborate research of a chemist like Faraday or Dumas.

A meagre, tabular view of work done, full of chemical symbols introduced without reference to their quantitative chemical meaning, but solely in order to save a few seconds of time and a few millimetres of space, is not sufficient. The essential points in each experiment, and the inferences deducible from it, should be put down in plain logical English as soon as possible after the experiment has been made. Many moments of spare time, while a precipitate is being washed or an evaporation is going on, will be found available for writing; while, if all description is deferred until the analysis is com-

pleted, there is great danger that some steps will escape the memory¹.

2. Do not jump to conclusions too quickly, or desert the regular course of testing, unless some absolutely characteristic reaction (such as the formation of liquid globules of mercury, or of violet vapours of iodine) is obtained.

The shortest way very often proves the longest, and *vice versa*, in analytical work.

3. Learn to distinguish between slight precipitates, changes of colour, &c., due to impurities in the salt, and reactions which indicate the nature of the salt itself.

Comparatively few single substances are met with in a state of absolute chemical purity, and reactions which are due to admixture of traces of other substances must be carefully distinguished from those which are due to the principal substance. In cases where the subject of examination is a solid, it will be easy to infer roughly what amount of a precipitate should be obtained from the known quantity of it which has been taken to form the solution; and when a liquid is being examined, the amount of residue obtained by evaporating a known volume of it, or the bulk of any precipitate previously obtained, will be an indication of its strength. If, then, the addition of a reagent merely causes a turbidity in a solution which is known to be strong, it would be inexcusable thoughtlessness to take such a result as indicating the general constitution of the substance.

✓ For instance, ordinary sodium carbonate invariably contains a little sulphate, and will, therefore, when tested with barium chloride, give a white precipitate which is not wholly soluble in hydrogen nitrate. But the amount of the insoluble residue will be obviously disproportionate to the amount of the salt known to be present in the solution, and hence, while the fact is observed and recorded, the examination for another radicle is to be proceeded with.

¹ An attempt is made at the end of this Part (Sect. VI) to give an example of the way in which an account of the analysis of a single salt should be written out, and to this the student should refer before he begins his analytical work.

Again, ordinary zinc generally contains a little lead and iron; and hence in applying the hydrogen sulphide test the solution may become more or less dark; also in applying the ammonium sulphide test, the precipitate may not be quite white, owing to the admixture of a trace of iron sulphide.

Such substances are always most safely analysed by the methods given for mixtures; but careful observation of the character and quantity of the precipitate ought generally to prevent the student from going astray.

4. Do not apply tests recklessly. Before adding a reagent, consider what substances are already known to be present in that which is being examined, and in what way the use of too much or too little of the reagent may affect the result.

If, for instance, hydrogen chloride has been used to dissolve the substance, it would be an absurd error to test for a chloride in that solution.

Similarly, when in the course of analysis ammonium salts have been added to the solution, it is easy, but not worth the trouble, to detect subsequently the presence of ammonium in the liquid.

Some indication is usually given of the amount of the reagent which should be used. It is, in general, easier to rectify the mistake of adding too little than that of adding too much.

An excellent way of making sure that a test has been applied rightly, is the following:—If no positive result has been obtained by it, add a drop of a solution of the substance which is being tested for. If the proper reaction is now obtained, the test must have been correctly applied for the detection of the substance; and the latter could not have been present in the original solution.

[No analytical Tables (with the exception of those which show the distribution of the radicles into groups) are included in this volume; not because such tables are considered of no value, but from a conviction that they will be best made by the student himself, in the same way as a summary of the contents of a book, or a *précis* of a document, rather as a result of intelligent work than as an introduction to it.]

SECTION II.

PRELIMINARY EXAMINATION OF THE SUBSTANCE.

[If it is a liquid pass on to p. 500.]

A. The Substance for Examination is a Solid.

General characters of the Substance.

- I** Examine and note down the physical characteristics of the substance; its colour, shape, crystalline form (if any), hardness, metallic or non-metallic appearance, &c. If it is brittle and in a single lump, break some of it into small fragments in a mortar, or by wrapping it in a fold of clean paper and striking it with a hammer on an anvil. Reduce these fragments to a very fine powder in the mortar, which should not be of glass unless the substance is a friable salt¹. The powdered substance may be conveniently kept in a small dry test-tube, fitted with a cork.

Effect of solvents upon the Substance.

[The following points should be borne in mind :—

1. In treating a single substance with a solvent, one of three things may happen.—(a) It may dissolve entirely. (b) It may not dissolve or be altered at all. (c) It may be decomposed, yielding new compounds, one or more of which may dissolve.

2. Reserve about one-fourth of the substance, in case of accidents.

3. Before the main portion is dealt with, it is advantageous to try the effect of solvents on a *very small* quantity.

4. Instead of using a large quantity of the solvent at once, it is best to take successive small portions, pouring off the solution

¹ For pulverising minerals, an agate mortar should, if possible, be used.

when the action becomes slow, then adding a little more of the solvent, heating, again pouring off, and so on.

5. If the substance enters readily into solution, it will be, on the whole, best to pass on at once to Sect. III. (p. 505), and to return to this Section, par. 8 &c., for confirmatory testing.

6. If the substance dissolves slowly, while the action is proceeding you may pass on to 8 (p. 489) and try the experiments mentioned in that and the following paragraphs.]

A. The substance has not a metallic appearance.

[If it has a bright metallic lustre, pass on to 7 (p. 488).]

1 **Solution in water.** Place about 0.5 grm. of the powdered substance (as much as will lie on the broad end of a spatula) in a test-tube, pour on it about 20 c.c. of water, and heat the liquid to boiling, shaking it occasionally¹. The tube may be supported on the sand-bath resting in a ring of the retort-stand, and while it is being gradually heated, you may proceed to heat some of the substance in an ignition tube, p. 489. If, by the time you have done this, the substance has dissolved, proceed to examine the solution at once; blowpipe experiments, &c., may be made afterwards as confirmatory tests.

A. The substance is entirely dissolved.

Filter the solution, if necessary, from any suspended particles of dirt, and examine it as directed in 14 (p. 501).

B. The substance is not dissolved, or at least not wholly (see notes ¹ and ²).

Allow the particles to subside, decant the liquid carefully, and boil the residue with a fresh quantity of water. If it

¹ Some acetates, tartrates, &c., are decomposed when boiled with water, a basic salt being formed: but this will dissolve in an acid. If, however, on boiling the substance alters in appearance, leaving a flocculent residue, it will be well to see whether it will not dissolve better in cold water.

² The best way of ascertaining whether any of the substance has been dissolved is to filter off a few drops of the liquid and evaporate it to dryness in a watch-glass. If a residue is left, something must have been dissolved by the water. But since nearly all carbonates are insoluble, it will generally be sufficient to add to the clear liquid, filtered or decanted, a few drops of solution of sodium carbonate. If no precipitate occurs, the substance is almost certainly insoluble, unless it is a salt of arsenic or of a metal belonging to Group VI.

dissolves, add this solution to the first portion, and proceed to 14. If it does not dissolve, pass on to the next paragraph.

- 3 Solution in dilute hydrogen chloride. Pour off the greater part of the liquid and add to the residue (or to a fresh portion of the original substance moistened with a little water) about eight or ten drops of concentrated hydrogen chloride, and if it does not dissolve, heat the mixture to boiling. If any gas having very decided characters, such as smell or colour, is evolved, refer to par. 12 (p. 497), and ascertain the nature of the evolved gas at once, by means of the tests there given.

- A The substance is dissolved by the hydrogen chloride. Dilute with about 20 c.c. of water (if any precipitate occurs, refer to 4 A, below) and examine the solution as directed in 18.
- B The substance is not dissolved by the hydrogen chloride. Pass on to the next paragraph.

- 4 Solution in concentrated hydrogen chloride. Take a fresh portion of the substance, add 5 or 6 c.c. of concentrated hydrogen chloride, and heat it to boiling, noting the character of any gas which may be evolved¹ (other than vapours of hydrogen chloride) and testing it as directed in par. 12.

- A The substance is dissolved.

Dilute the solution with about 20 c.c. of water, and examine it as directed in 18. [If any precipitate is produced on dilution, add strong hydrogen chloride, drop by drop, and warm the liquid until it disappears (see note²).]

¹ Concentrated hydrogen chloride will often, in the case of sulphides, chromates, and cyanides, produce an evolution of gas, where the dilute acid has failed to do so.

² It may be due to the presence of BISMUTH or ANTIMONY, since their chlorides are decomposed by water; but the precipitate will pretty readily dissolve when strong acid is added.

It may, perhaps, be due to LEAD; since lead chloride is much less soluble in cold water than in hot, and the addition of water will have cooled the solution. In this case the precipitate will redissolve when the liquid is warmed, and will be reprecipitated in needle-like crystals as it again becomes cool; a reaction very characteristic of lead.

✓ Silver chloride, it may be noted, is slightly soluble in strong hydrogen chloride, but is thrown down on dilution.

- B** The substance appears to be acted upon, but there is a residue left, different in appearance to the original salt.

Allow the residue to subside, pour off the solution and examine it, after¹ dilution with about 20 c.c. of water, as directed in 18. If the residue does not subside quickly, add to the solution about twice its volume of water (that it may not act on the filter), filter it, and proceed to 18.

The residue may consist of—

- (a) SULPHUR. If so, it will be yellowish white, and remain long in suspension, being more easily filtered off after long boiling. It indicates the presence of a PERSULPHIDE, in which case hydrogen sulphide will have been evolved (see 12 F); or of a THIOSULPHATE, in which case sulphur dioxide will have been evolved (12 D).
- (β) HYDROGEN SILICATE, which is a white gelatinous substance, and will have been formed from the decomposition of a SILICATE. Wash the residue on a filter, dry it at a gentle heat, and heat some of it in a bead of microcosmic salt, as directed, p. 311. If it is silica it will float undissolved in the bead, and the original substance may be inferred with certainty to be a silicate.
- (γ) The residue may also be a chloride of one of the metals in Group I. If so, it will be a dense white substance, and will turn black when a drop of ammonium sulphide is added. The original substance should be dissolved in hydrogen nitrate, as directed below (θ).

- C** The substance is unacted upon by concentrated hydrogen chloride.

Pass on to the next paragraph.

- 5** Add three or four drops of strong hydrogen
 Solution in nitrate to the solution containing hydrogen
 aqua regia. chloride, and boil the liquid¹.

- A** The substance is dissolved.

Boil the liquid until no more chlorine is evolved, dilute with 20 c.c. of water, and examine the solution as directed in 18.

- B** The substance is not dissolved. Pass on to the next paragraph.

¹ This should be done in a draught-cupboard, if possible, since chlorine is evolved.

- 6 **Solution in hydrogen nitrate.** Boil a fresh portion of the substance with dilute hydrogen nitrate, and, if it does not dissolve, with strong hydrogen nitrate.

If a clear solution is obtained, evaporate it down until all excess of acid is removed, dilute it with water, and test it as directed in 17.

If the substance remains undissolved, even after the addition of three or four times its volume of water¹, it must be examined as directed in Sect. V.

B. The substance has a metallic appearance.

[If, besides having a bright lustre, it is malleable, it is certainly a metal.

If it is brittle, it may be one of such minerals as galena, antimonite, iron pyrites, graphite, &c.]

- 7 **Solution of a metal in hydrogen nitrate.** Place a little of it (powdered, if possible) in a test-tube, add a few drops of water and then about 5 c.c. of concentrated hydrogen nitrate, and (if no action begins) heat it to boiling.

A. The substance dissolves.

Drive off any excess of acid by evaporation, dilute the solution with about 20 c.c. of water (stopping if any precipitate is produced, which would be the case if bismuth is present), and examine it as directed in 17.

B. The substance does not dissolve, but it is converted into a white powder.

Add about 20 c.c. of water, and boil again.

If it dissolves, examine the solution as directed in 17.

If it does not dissolve, the original substance is probably tin, antimony, or a native sulphide, such as galena, antimonite, or pyrites. If of the latter class, the original substance will, when boiled with a little strong hydrogen chloride, give off hydrogen sulphide (tested for by lead acetate paper, par. 12 F).

Boil some of the original substance with aqua regia (using

¹ Some nitrates, e.g. barium nitrate, are insoluble in strong hydrogen nitrate, but readily dissolve when water is added.

very little hydrogen nitrate); dilute the solution with about three times its volume of water (not more, or antimony oxychloride may be precipitated); filter from any deposit of sulphur; and test the solution for metals, beginning at paragraph 18.

- C The substance is unacted upon. It is probably either GOLD or PLATINUM; gold if it is yellow, platinum if it is white. It will dissolve in aqua regia, and the solution should be examined as directed on p. 508.

[Graphite has a metallic appearance, and would be insoluble, even in aqua regia. See Sect. V, for the method of treating it.]

Effect of heat upon the substance.

[The following experiments should be begun while the solution of the substance is being made, in order to economise time. If no characteristic results are obtained at once, and if the substance has entered readily into solution, the blowpipe examination may be continued at intervals during the testing of the solution, e.g. while a filtration is going on, or a precipitate is subsiding, and the results will be applicable as confirmatory evidence.]

- 8 Substance heated in ignition tube. Place a small quantity of the substance in an ignition tube, and heat it over the Bunsen's burner, at first very gently, then to redness, and afterwards before the blowpipe to a temperature as high as the tube will bear.

- A The substance has a metallic lustre and readily fuses.

It must be lead, cadmium, bismuth, antimony, tin, or zinc. Pass on to 10.

- B The substance does not fuse, even when heated to redness, and gives off no gas, vapour, or sublimate, but changes colour.

(a) *From white to yellow, becoming white on cooling.* It is ZINC OXIDE, TIN DIOXIDE, or BISMUTH TRIOXIDE (probably the last, if it fuses at a strong red heat). Pass on to 10.

(β) *From red to black, turning red again on cooling.* It is probably IRON PEROXIDE. Pass on to 9 B.

- C The substance fuses at a very moderate heat, and possibly gives off water (of crystallisation)

Wipe the inside of the tube perfectly dry with twisted slips of blotting-paper, and when no further moisture is condensed, raise the temperature, and observe which of the following results takes place.

- D The substance volatilises entirely, or, at any rate yields a distinct sublimate. It is a salt of AMMONIUM, ARSENIC, or MERCURY; or possibly HYDROGEN OXALATE, or SULPHUR. Observe the character of the sublimate in the tube.

(a) *It is white and amorphous.* The substance is an AMMONIUM salt, or a MERCURY salt (not, however, mercury iodide or sulphide, since these are coloured). Pass on to 9 A.

(β) *It is white and crystalline.* The substance is probably ARSENIC TRIOXIDE, see fig. 93, p. 366 (or if the crystals are slender prisms, HYDROGEN OXALATE). Pass on to 9 A.

(γ) *It is yellow, the original substance being red, and fusing to a nearly black liquid before volatilising. The sublimate becomes red when touched with a wire or glass rod.* The substance is MERCURY IODIDE, see note¹).

(δ) *It is yellow and amorphous, the original substance being also yellow.* It is ARSENIC SULPHIDE. Pass on to 9 A.

(ε) *It forms liquid drops with metallic lustre.* It is mercury, and the substance is a MERCURY salt. Examine for the non-metallic radicle as directed in 12, and Sect. IV (25).

(ζ) *It forms brownish yellow, transparent drops, which do not solidify for some time.* It is SULPHUR (but see note²).

To make sure that the sublimate consists of sulphur, cut off the closed end of the tube, and heat the sublimate gently, holding the tube in a slanting position. If it is sulphur, it will be oxidised in the current of air, and sulphur dioxide will be formed, which may be recognised by its smell and by its acid reaction on litmus-paper held at the upper end of the tube.

¹ This reaction is so characteristic of mercury iodide that the substance may be at once examined for mercury and iodine. For this purpose, a little of the substance should be decomposed by boiling it with some solution of potassium hydrate, as directed in Sect. V. par 35.

² Red phosphorus gives a sublimate of ordinary phosphorus, identified by its inflammability.

The original substance is either SULPHUR itself (easily recognised by its physical properties, see p. 267), a PERSULPHIDE (*e.g.* Pyrites) or a THIOSULPHATE. These latter will be examined for in the ordinary course. Pass on to **9 B**.

E The substance becomes charred, i.e. turns black, and leaves a carbonaceous residu, while vapours are evolved which have a strong smell like burnt paper. It is an ACETATE, TARTRATE, OXALATE, or other organic salt (see, however, note below¹). These will be examined for in the ordinary course. Pass on to **9 B**.

F The substance does not become charred, but evolves a gas, with or without previous fusion. Examine the character of the gas as directed below, and then pass on to **9 B**.

The gas evolved is,—

(a) *Colourless, and has the peculiar suffocating smell of sulphur dioxide, and reddens a piece of blue litmus-paper held in the mouth of the tube.* This indicates the presence of a THIOSULPHATE or a SULPHATE decomposable by heat.

(b) *Colourless, and has the peculiar smell of cyanogen, resembling essence of almonds.*

Hold a lighted match to the mouth of the tube. If the gas burns with a pink flame, a CYANIDE or FERROCYANIDE is present.

(γ) *Colourless and odourless.*

Place a single drop of lime-water on a watch-glass, and hold it close to the mouth of the tube (which should be as far as possible from the lamp-flame). If the drop becomes turbid, the gas is CARBON DIOXIDE, and proceeds from the decomposition of a CARBONATE or an OXALATE.

If carbon dioxide is not detected, drop a small splinter of charcoal from the charred end of a match into the tube, add a little more of the substance, and again heat the bulb. If the

¹ Some other substances, *e.g.* COPPER CARBONATE, COPPER NITRATE, MANGANESE CARBONATE, turn black when heated, but do not evolve organic vapours. To obtain a further proof that the substance is organic, the black residue may be heated again with addition of a small quantity of potassium nitrate, when, if it is organic, the blackness will disappear, with slight deflagration.

charcoal burns vividly, the gas is oxygen and the substance is a CHLORATE, NITRATE, NITRITE, CHROMATE, or PEROXIDE¹.

- (d) *Orange-coloured, and reddens litmus-paper.* The substance is probably a NITRATE or NITRITE; if so, a splinter of charcoal dropped into the tube will deflagrate as in the case of chlorates. Some few bromides and iodides are decomposed by heat alone, and give off orange vapours of bromine, which condense to an orange liquid, or violet vapours of iodine, which condense in the form of steel-gray flakes.

[Hypophosphites, when heated, give off hydrogen phosphide, which inflames spontaneously at the mouth of the tube.]

- G *The substance remains unaltered, or simply fuses, when heated to redness.* It is probably a salt of an ALKALI METAL, or BARIUM-, STRONTIUM-, or CALCIUM-CHLORIDE.

Pass on to 9 B.

- 9 The course next to be followed will depend upon the appearance of the substance and the results obtained by heating it in a tube.

- A *The substance yielded a sublimate in the tube.*

Reduction in tube. Mix a small quantity of the original substance intimately with twice as much anhydrous sodium carbonate, introduce into an ignition tube enough of the mixture to half fill the bulb, put over it a layer of sodium carbonate and heat it slowly over the lamp. If any moisture condenses, wipe the tube dry and clean with slips of blotting-paper.

- (a) *A bright metallic sublimate is formed, which may be seen with a magnifier to consist of liquid metallic globules.* The substance is a MERCURY salt.

To make quite sure of the character of the sublimate, pass down into the tube a thin slip of wood, such as a match, and scrape together the sublimed metal. If it is mercury, the particles will run together into one large globule, which may be allowed to drop into a watch-glass. Proceed to examine for the non-metallic radicle as directed in 12, and Sect. IV. (25).

¹ AMMONIUM CHROMATE, however, gives off, not oxygen, but water and nitrogen, and a light, bulky, olive-green residue of chromium oxide is left. AMMONIUM NITRATE, moreover, gives off nitrogen monoxide, often with a slight explosion.

(β) *The sublimate is a nearly black, but lustrous mirror.* The substance is an ARSENIC salt.

Break off the tube close to the bulb, hold it horizontally, and slowly heat the part containing the sublimate over a lamp with a very small flame. If the deposit is arsenic, it will readily volatilise and become oxidised, condensing in the cool parts of the tube in sparkling transparent crystals of arsenic trioxide (for the form of these refer to p. 366).

If such a characteristic result is obtained, you may proceed at once to examine for the non-metallic radicle as directed in 12 and Sect. IV. (25).

If neither mercury nor arsenic is found, and if the sublimate is white and amorphous, the substance may be examined at once for ammonium, as directed in 24, and then for the non-metallic radicle (12 and 25).

B *The substance did not volatilise, and is coloured.* If so, it is very probable that it will impart colour to a borax bead.

Examination Fuse some borax in a loop of platinum wire, in borax bead. as directed on p. 100, and when a clear transparent bead has been obtained, bring into it a minute portion of the powdered substance and heat it first at the tip of the blowpipe flame, then in the oxidising flame, and lastly in the reducing flame. If no colour is imparted to the bead, pass on to the next paragraph. If the bead becomes coloured, observe its character, and then pass on to 12.

(α) *It is blue, in both oxidising and reducing flames.* The substance is a COBALT salt.

(β) *It is greenish blue in the oxidising flame, and becomes almost colourless in the reducing flame. If much of the substance has been added, the bead becomes red and opaque in the reducing flame.* The substance is a COPPER salt.

(γ) *It is green, both in the oxidising and reducing flame.* The substance is a CHROMIUM salt, or a CHROMATE.

(δ) *It is orange-red in the oxidising flame, becoming light yellow as it cools. In the reducing flame it is orange while hot, and dull bottle-green when cold.* The substance is an IRON salt.

- (e) *It is amethyst-red in the oxidising flame, and becomes quite colourless in the reducing flame.* The substance is a MANGANESE salt.
- (f) *It is brownish red in the oxidising flame, and becomes gray and turbid in the reducing flame.* The substance is a NICKEL salt.

C The substance is colourless, or if coloured has given no reaction with a borax bead, and is infusible, or difficultly fusible.

Pass on to the next paragraph.

- 10** Reduction on charcoal. Mix a small portion of it with an equal quantity of potassium cyanide, and heat it cautiously (since nitrates may deflagrate) on charcoal, as directed on p. 102.

[The substance should be held just within the tip of the blowpipe-flame, and the blast should be pretty strong. As we have such powerful reducing agents present as potassium cyanide and charcoal, we can afford to sacrifice some of the reducing power of the blowpipe-flame itself, for the sake of getting as high a temperature as possible.]

If no characteristic result is obtained, pass on to 11.]

- A** A white residue or incrustation is left on the charcoal. [If this residue is infusible and strongly luminous while held in the blowpipe-flame, ALUMINIUM, ZINC, MAGNESIUM, STRONTIUM, or CALCIUM is probably present.]

Moisten the residue with one small drop of solution of cobalt nitrate, and heat it again strongly for a few seconds. If on cooling the residue has a blue colour, ALUMINIUM is probably present (see, however, note 1, p. 431); if it has a faint pink tinge, MAGNESIUM is present; if it is green, ZINC is present.

- B** Bright metallic globules are obtained.

Continue the heat, with addition, if necessary, of a little more potassium cyanide, until the small globules have run together into one large one, and the flux has disappeared. When the metal is cool¹, detach it from the charcoal with a knife, and

¹ The cooling may be hastened by very cautiously dropping water upon the charcoal at a little distance from the cavity, not into the cavity itself.

try its malleability, as directed on p. 103, noting also if any incrustation has formed on the charcoal in or around the cavity¹; then pass on to 12.

(a) *The metallic globule is malleable, with brilliant lustre, and there is no incrustation on the charcoal.* The substance is a SILVER salt.

(β) *The globule is malleable, and a slight white incrustation is formed on the sides of the cavity.* The substance is a TIN salt.

(γ) *The globule is malleable and soft, and a yellow incrustation is formed on the charcoal.* The substance is a LEAD salt.

(δ) *The globule is brittle, and white fumes ascend from it while hot; a white incrustation is formed on the charcoal.* The substance is an ANTIMONY salt.

(ε) *The globule is brittle, and a yellow incrustation is formed.* The substance is a BISMUTH salt².

C *No globule is obtained, but a reddish brown incrustation is formed on the charcoal.* The substance is a CADMIUM salt.
Pass on to 12.

[If no characteristic result has been obtained it may be worth while to examine the substance in a borax bead, as directed in 9 B.]

11 Colour imparted to flame.³ Moisten the end of a *perfectly clean* platinum wire with strong hydrogen chloride³, dip the wire into the powdered substance, and hold it at the edge of the flame of a Bunsen's burner. Observe the colour, if any, imparted to the flame (see next page), and also see whether the colour is altered when a piece of rather deep blue glass is interposed between the eye and the flame. Then pass on to 12.

¹ Care must be taken not to mistake the white ash, which charcoal always leaves when burnt, for an incrustation of metallic oxide. The former is light, almost downy, in appearance; the latter is more compact, and generally has a definite border.

² The globule of bismuth, although in reality brittle, does not always crumble to pieces under the pestle or hammer; the particles may remain aggregated so as to appear not unlike a flattened plate of malleable metal. But the edges of the plate are always jagged, as may be readily seen with a magnifier, and a blow or two of the pestle is generally sufficient to break it into several pieces.

³ This should always be done, since metal-chlorides are more volatile than other salts.

[It must be borne in mind that traces of sodium are almost invariably present in a substance, and that the intense yellow flame due to its presence will often mask other colours. This difficulty is especially felt in the case of potassium salts; the barium, strontium, and calcium salts are so much less volatile that they remain long after the traces of sodium have volatilised. A transient yellow tinge will almost always be imparted to the flame when the salt is first introduced into it; and when this has passed away, the other characteristic colours should be looked for.]

- A It is yellow, nearly invisible through blue glass. SODIUM is present.
- B It is crimson, unaltered through blue glass. STRONTIUM is present.
- C It is orange-red, greenish-gray through blue glass. CALCIUM is present.
- D It is green, unaltered through blue glass. BARIUM, COPPER, or a BORATE is present.
- E It is lavender, crimson through blue glass. POTASSIUM is present.
- F It is bluish-gray, unaltered through blue glass. LEAD, ARSENIC, or ANTIMONY may be present.

It will be safest not to consider these results as absolutely decisive of the nature of the substance (since small traces of the above elements are sufficient to colour flame intensely), but to pass on to 12, and refer to the flame-colour only as a confirmatory test.

Action of strong hydrogen sulphate upon the substance.

- 12** Put a little of the substance, just moistened with water, (or of the concentrated solution) into a test-tube, add cautiously 1 or 2 c.c. of strong hydrogen sulphate, and warm it gently and gradually, if no action begins at once. If no action occurs, pass on to 17. If any characteristic gas or vapour is given off, observe its properties.

- A *It is colourless, has no distinctive smell, and is incombustible.*

It is carbon dioxide, and shows that the substance contains a CARBONATE¹.

To make sure that the gas is carbon dioxide, lower into the tube a pipette having a drop of lime-water in it, and gently suck a little of the gas through it (p. 195). If the lime-water becomes cloudy, the gas is certainly carbon dioxide. Pass on to 17.

- B *It is colourless, inodorous, and burns with a blue flame.*

It is carbon monoxide, and points to the presence of an OXALATE or FERROCYANIDE. These will be detected in following the usual course. Pass on to 17.

- C *It has a faint sweetish smell like essence of almonds.*

It is hydrogen cyanide, and indicates a CYANIDE, or other cyanogen compound.

To make sure that the gas is hydrogen cyanide, put a few drops of solution of potassium hydrate into a small porcelain dish, soak in it part of a folded strip of blotting-paper, place the moistened paper in the test-tube and leave it there for a minute, warming the mixture at the bottom of the tube to obtain more gas. Any hydrogen cyanide present will be absorbed by the potash.

Replace the slip of blotting-paper in the dish, add 2 or 3 c.c. of water and stir it in order to extract any potassium cyanide formed. Then pour the solution into a test-tube and (1) add 2 or 3 drops of solution of iron protosulphate, shake up, and warm the mixture; then (2) add excess of dilute hydrogen chloride. If the acidified liquid turns greenish blue or gives a blue precipitate, the evolved gas was certainly hydrogen cyanide.

If the presence of hydrogen cyanide is thus proved, it will be advisable to decompose the substance and obtain the metal as a nitrate before proceeding to examine for it. If this has not already been done in the process of dissolving the substance,

¹ It should be noted that many substances, e.g. potassium hydrate, potassium silicate, manganese dioxide, and various minerals, are liable to contain a carbonate as an impurity (see Rule 3, p. 482).

boil about a gramme of the substance (or 20 c.c. of the solution) with excess of strong hydrogen nitrate in a dish until all hydrogen cyanide is expelled, dilute with 20 c.c. of water, and proceed to 17.

D *It has a sharp, penetrating smell, like that of burning sulphur.*

It is probably sulphur dioxide, and indicates a SULPHITE or THIOSULPHATE (see, however, note¹).

To make sure that it is sulphur dioxide, put two or three drops of solution of potassium chromate into a watch-glass, add a drop of strong hydrogen chloride, dip a bit of white blotting-paper into the solution, and lay it upon the mouth of the test-tube. If the red solution turns green in a minute or so (see p. 425), the gas is certainly sulphur dioxide.

If it is so, the presence of one of the above-mentioned radicles may be confirmed at once as follows.

Add to a little of the original solution of the substance a few drops of dilute hydrogen nitrate. If this produces a milky precipitate in the course of a minute or so, a THIOSULPHATE is present. If not, a SULPHITE is present.

In either case, add a little of the liquid to some blue starch iodide (made as directed in expt. 3 b, p. 283²). If the colour disappears, the presence of a sulphite or thiosulphate is confirmed.

If either is found, it will be advisable to separate it, and obtain the metal as a chloride, before proceeding to detect it by the usual course. To do this, add 2 or 3 c.c. of strong hydrogen chloride to about a gramme of the substance (or 20 c.c. of the original solution) and evaporate to dryness in a dish: warm the residue with about 20 c.c. of water, filter, if necessary, from sulphur, and test the filtrate (which contains the metal as chloride) by the usual course, beginning at 18.

¹ If the gas is only given off at a high temperature, and especially if the substance turns black, the evolution of sulphur dioxide is due to the decomposition of the hydrogen sulphate itself by some reducing agent, e.g. a tartrate.

² Instead of this, solution of potassium permanganate may be used, if at hand. Sulphites and thiosulphates quickly and wholly destroy the intense purple colour of this solution (see p. 418).

- E** It has a pungent, acid smell, and reddens blue litmus, but does not give the reaction of sulphur dioxide (see last paragraph).

It is hydrogen chloride, acetate (if it smells like vinegar), or fluoride (if any corrosion of the glass is perceptible).

If the glass is decidedly acted on, and if a moistened glass rod held in the tube becomes coated with a white crust of silica (p. 313), a fluoride may be at once tested for as directed in 33, p. 523.

The other radicles will be detected in following the ordinary course. Pass on to 17.

- F** It has an offensive smell, like rotten eggs, and blackens a piece of blotting-paper moistened with lead acetate and laid on the mouth of the tube.

It is hydrogen sulphide, and indicates the presence of a SULPHIDE.

It will be advisable to obtain the metal as a chloride before proceeding to examine for it in the usual course. Unless this has been already done in the process of dissolving the substance (3 and 4, p. 486), add 2 or 3 c.c. of strong hydrogen chloride to about 2 grammes of the substance (or 20 c.c. of the original solution); boil in a dish until all hydrogen sulphide is expelled; filter from deposited sulphur (if any) and examine the filtrate, which contains the metal as chloride, as directed in 18.

- G** It is greenish, has the smell of chlorine, or chlorine tetroxide, and bleaches wetted litmus-paper held in the tube.

The substance is a HYPOCHLORITE or CHLORATE (the latter if the characteristic sweetish smell of chlorine tetroxide is observed, and the liquid turns orange).

[If the gas is the result of the action of hydrogen chloride (par. 3) and not hydrogen sulphate, the evolution of chlorine points to the presence of an oxidising substance, such as a NITRATE, NITRITE, CHROMATE, or PEROXIDE. The three former will be detected in the usual course; if the substance is a PEROXIDE it will give off oxygen when heated in an ignition-tube (8 F 7).]

To see if a hypochlorite is present, add to a little of the original solution of the substance enough potassium hydrate

to render it alkaline, then a few drops of solution of lead acetate, and boil the mixture. If the white precipitate of lead hydrate turns brown, a hypochlorite is present. The indigo sulphate test (p. 163) may be also tried.

If it is not found, a chlorate should be examined for as directed in 28, p. 521. Then pass on to 17.

H *It is orange, and reddens blue litmus.*

It is nitrogen tetroxide, and indicates a NITRITE.

To confirm this, test a little of the original solution of the substance with iron protosulphate. If a black liquid is obtained, turning yellow with effervescence when boiled (p. 169), a nitrite is certainly present. Pass on to 17.

[Nitrates are liable to yield some nitrogen tetroxide when heated with strong hydrogen sulphate; they will be examined for in the ordinary course. But if the gas was given off readily and without application of heat, the substance is certainly a nitrite.]

I *It is red, and bleaches wetted blue litmus.*

It is bromine, and indicates a BROMIDE. This will be examined for in the ordinary course. Pass on to 17.

K *It is violet, and solidifies in black crystals.*

It is iodine, and indicates an IODIDE. This will be examined for in the ordinary course. Pass on to 17.

B. The Substance for Examination is a Liquid.

[Reserve about one-fourth, in case of accidents.]

13 Observe and note down the colour and smell (if any¹) of the liquid.

Place about 2 or 3 c.c. of the liquid in a watch-glass and set it on the sand-bath to evaporate to dryness, while other experiments with the solution are proceeded with.

The residue, if any, should be examined by heating in an ignition-tube and before the blowpipe according to the directions already given (par. 8), and if the nature of the liquid has been

¹ A cyanide, for instance, may often be detected by the smell of hydrogen cyanide which it gives off; some sulphides by the smell of hydrogen sulphide; hydrogen acetate by the smell of vinegar; free ammonia by its characteristic smell.

discovered before the residue is obtained, the results of the blowpipe examination will serve as confirmatory evidence.

If the liquid volatilises without leaving any residue, and if the presence of a hydrogen salt is found (15 B), pass on to Sect. IV, p. 517, since no metal (other than hydrogen) is present.

- 14 *Colour imparted to flame.* Dip a *perfectly clean* platinum wire into the solution, and hold it at the border of the flame of a Bunsen's burner. If any characteristic colour is imparted to the flame, refer to 11 (p. 495). Then return to 15.

- 15 *Reaction on litmus-paper.* Take out a drop on a glass rod and place it upon a piece of **blue litmus-paper**. If no effect is produced, place another drop upon a piece of **reddened litmus-paper**.

A *The liquid is neutral, or nearly so, to test-paper.*

Examine a small portion of it with hydrogen sulphate as directed in 12 (p. 496).

B *The liquid reddens blue litmus-paper strongly.*

This may be due to the presence either of a HYDROGEN salt or of a double salt of HYDROGEN and a METAL, or lastly of certain metallic salts, *e.g.* COPPER or MERCURY salts, which, although containing no basic hydrogen, have an acid reaction.

To distinguish between these, place a little of the liquid in another test-tube, add a drop of solution of sodium carbonate on the end of a glass rod, and stir the mixture. If no precipitate is produced, or the precipitate redissolves immediately, with effervescence, a HYDROGEN salt is present. If a permanent turbidity is produced, the acid reaction is due to the presence of a metallic salt, soluble in water. • Pass on to 17.

C *The liquid turns reddened litmus-paper strongly blue.*

This may be due to the presence of a BORATE, PHOSPHATE, NITRITE, SILICATE, HYDRATE, CARBONATE, SULPHIDE, or CYANIDE.

Examine a small portion of the solution with hydrogen sulphate as directed in 12, which will ensure the detection of a CARBONATE, CYANIDE, SULPHIDE, or NITRITE, if present.

If a carbonate or nitrite is detected, pass on to 17.

In all other cases proceed as directed in the next paragraph.

- 16 Action of hydrogen nitrate on alkaline solutions. Pour a little of the solution into a test-tube, and add dilute hydrogen nitrate, drop by drop, until the liquid is strongly acid; then warm, but do not boil, the mixture. Observe whether any gas is evolved, or precipitate formed, or both.

[If the original solution was yellow, and becomes red when the acid is added, a CHROMATE is present.]

A No precipitate or evolution of gas occurs.

The substance is probably a BORATE, PHOSPHATE, or HYDRATE; possibly a SILICATE.

Add a little of the original alkaline solution to some solution of ammonium chloride in a test-tube, and heat it. If a *white gelatinous precipitate insoluble in hydrogen chloride* is formed, a SILICATE is present¹, and about 20 c.c. of the original solution should be evaporated with hydrogen chloride as directed just below (B).

If no precipitate is formed, pass on to 17.

B No gas is evolved, other than mere acid vapours of hydrogen nitrate itself, but a white gelatinous precipitate is formed, which does not redissolve in excess of acid.

The solution contains a SILICATE of an alkali-metal.

Put about 20 c.c. of the original solution into a dish, add a slight excess of strong hydrogen chloride, and evaporate the whole to complete dryness, continuing the heat, with occasional stirring, until the residue loses all gelatinous appearance. Warm it with a little water, grinding the whole together with a pestle: then filter. Test the solution for an alkali-metal as directed in 24. Wash the residue of silicon dioxide on the filter, dry it, and fuse a little of it in a bead of microcosmic salt (p. 311). If it floats undissolved in the bead it is silicon dioxide, and the original substance is proved to be a silicate.

C No gas is evolved, but a precipitate is formed which redissolves in the excess of hydrogen nitrate.

¹ A solution of potassium aluminate would give a precipitate of aluminium hydrate; but this will readily dissolve in excess of hydrogen nitrate.

The substance contains one of the metals which form soluble double oxides or hydrates with an alkali-metal¹.

Pass on to 17, bearing in mind that an alkali-metal must be sought for, as well as one of the others above mentioned, and therefore that the latter must be separated by addition of the proper group-reagent in excess, and the filtrate examined for the alkali-metal.

- D** *Hydrogen cyanide is evolved* (as will have been detected and confirmed in the examination with hydrogen sulphate, par. 12), and,

(a) *No precipitate is formed.*

The solution contains a CYANIDE of an alkali-metal.

Boil about 10 c.c. of the original solution in a dish with excess of hydrogen chloride until all hydrogen cyanide is expelled, and test the solution for an alkali-metal, as directed in 24.

(β) *A precipitate is formed.*

The solution contains a double CYANIDE of an alkali-metal with some other metal.

Evaporate about 20 c.c. of the original solution to dryness, and boil the residue with 6 or 8 c.c. of strong hydrogen nitrate, which will decompose all the cyanides present. When all hydrogen cyanide has been expelled, dilute the solution with 20 c.c. of water, and examine it in the usual way for the two metals, beginning at 17; remembering that, when one metal has been found, the group reagent must be added in excess to another portion of the solution, in order to separate it entirely. The liquid must then be filtered, and the filtrate tested for an alkali-metal, 24.

- E** *Hydrogen sulphide is evolved* (as will have been detected in the examination with hydrogen sulphate, par. 12), and

(a) *No precipitate is formed.*

The solution contains a SULPHIDE of one of the metals in Group IV, V, or VI. Treat about 20 c.c. of the original solution as directed just below, in β.

(β) *A white milky precipitate is formed.*

The solution contains a POLYSULPHIDE of one of the metals in Group IV, V, or VI.

¹ A list of these metals is given at the foot of the Table of Solubilities, Appendix E.

Add excess of dilute hydrogen chloride to about 20 c.c. of the original solution; boil in a dish until all hydrogen sulphide is expelled; filter from deposited sulphur (if any) and examine the filtrate, which contains the metal as chloride, as directed in 22.

(γ) *A coloured precipitate is formed.*

The solution contains a double sulphide of an alkali-metal with arsenic, antimony, or tin.

Add a slight excess of dilute hydrogen chloride to about 20 c.c. of the original solution, warm and filter; test the filtrate for an alkali-metal as directed in 24. Wash the precipitate, dissolve it in strong hydrogen chloride with addition of a drop or two of hydrogen nitrate, and test the solution for arsenic, antimony, and tin as directed in 18.

SECTION III.

EXAMINATION OF THE SOLUTION OF A SINGLE
SUBSTANCE FOR A METAL.

[If the substance has been dissolved in hydrogen chloride, or aqua regia, pass on to 18, since silver salts and mercury protosalts cannot be present, and lead will be detected in the next group.]

1. Examination for the Metals included in Group I.

SILVER, MERCURY (monovalent), LEAD.

17 Hydrogen chloride test. Add dilute hydrogen chloride, drop by drop, to a portion of the cold solution. If a precipitate is obtained, add several drops of the strong acid, and apply heat, in order to ascertain if the precipitate is soluble in excess.

A No precipitate, or a precipitate which dissolves in excess of the acid, is obtained¹.

[If some of it reappears, on cooling the liquid, in needle-like crystals, it is lead chloride.]

SILVER salts, MERCURY protosalts, and also LEAD salts, unless the solution is very dilute, are absent. Pass on to 18.

B A permanent white precipitate is formed.

A metal belonging to Group I is present.

Add to the liquid containing the precipitate 2 or 3 c.c. of solution of ammonium hydrate, and shake it up.

¹ Such a precipitate will be probably due to the presence of a BISMUTH or ANTIMONY salt, since bismuth and antimony chlorides (which will be formed on addition of hydrogen chloride) are more easily decomposed by water than their other salts.

(a) *The precipitate is redissolved.*

SILVER is present. This may be also inferred if the precipitate is curdy and becomes gray on exposure to light. As a confirmatory test, add to another portion of the original solution (which, if acid, must be made neutral by ammonia) a drop of solution of potassium chromate, which will cause a crimson precipitate if silver is present.

(β) *The precipitate turns black.*

A MERCURY protosalt is present. To confirm this, place a clean strip of copper in another portion of the original solution, acidified, if necessary, with dilute hydrogen nitrate. If the copper is coated with a gray deposit, which becomes silvery-bright when rubbed with a cloth, and disappears when heated over a lamp, the presence of mercury may be considered certain.

(γ) *The precipitate remains unaltered in appearance.*

LEAD is present. To confirm this, test another portion of the original solution with dilute hydrogen sulphate: a white precipitate will be produced if lead is present.

[The precipitate may consist of silica, sulphur, or certain sulphides, if the original solution was alkaline. This, however, should have been already ascertained, see 16.]

2. Examination for the Metals included in Group II.

MERCURY (divalent), LEAD, COPPER, BISMUTH, CADMIUM, ARSENIC, ANTIMONY, TIN, GOLD, PLATINUM.

- 18 Hydrogen** Add to the portion of the solution which has sulphide test. been acidified with hydrogen chloride, solution of hydrogen sulphide; first a drop or two, shaking the mixture, and noting whether any precipitate is produced: if so, add more of the reagent until the liquid, after being well shaken, smells strongly of it; observe if the precipitate changes in colour (see note ¹).

¹ The precipitate produced in solutions of mercury persalts by the first drop of the solution of hydrogen sulphide is white, and quickly changes to yellow, brown, and finally black, on further addition of the reagent.

Salts of lead, if a large excess of hydrogen chloride is present, give a dull red precipitate of lead sulphochloride.

A No precipitate is formed.

None of the metals included in Group II are present. Pass on to 20.

B A perfectly white, milky precipitate is produced. This consists solely of SULPHUR, and is due to the decomposition of the hydrogen sulphide, by some oxidising substance present in the solution, probably a CHROMATE or an IRON PERSALT. If the solution is red or yellow, and turns light green simultaneously with the precipitation of sulphur, one of the above two substances is certainly present; they will, however, be detected in the course of examination for Group III (20), to which you should pass on.

[The decomposition of the hydrogen sulphide may also be due to the presence of CHLORINE (if aqua regia has been used to dissolve the substance), a HYPOCHLORITE, a CHLORATE, a NITRITE, or a SULPHITE. These will, however, have been detected in the preliminary examination. Record the result, therefore, but pass on to 20 as if the precipitate had not occurred.]

C The precipitate is light yellow.

CADMIUM, ARSENIC, or TIN (as persalt) is present.

Add to the precipitate (previously pouring off as much of the liquid as possible) solution of **potassium hydrate** (see note¹) in excess, and warm the mixture.

(a) The precipitate dissolves.

TIN (as persalt) or ARSENIC is present. To distinguish between them, add a few drops of ammonia to a portion of the original solution. If *a white precipitate is produced*, TIN is present; the reduction of the salt before the blowpipe (*malleable bead, white incrustation*) will afford confirmatory evidence. If *no precipitate is obtained*, ARSENIC is present.

If the presence of arsenic has not been already indicated in the preliminary examination (volatilisation and reduction in ignition tube, § A β), add to some of the original substance (or solution) 4 or 5 c.c. of solution of **potassium hydrate**, drop in a bit of *pure zinc* (see p. 369), lay on the mouth of

¹ The potassium hydrate used for this purpose must be fairly free from carbonate, otherwise tin sulphide, if present, will not entirely dissolve.

the test-tube a bit of white blotting-paper moistened with a drop of solution of silver nitrate, and heat the liquid in the tube to boiling. If the silver nitrate is blackened, arsenic is certainly present.

[If arsenic is found, the substance may be an ARSENITE or ARSENATE; if the latter, the precipitate caused by hydrogen sulphide will have formed only on boiling the liquid. Refer to p. 372, expt. 2, and p. 374, expts. 2, 3, for other means of distinguishing between them.]

(β) *The precipitate does not dissolve.*

CADMIUM is present. Confirm this inference by adding ammonia to some of the original solution, which should produce a white precipitate, soluble in excess, and precipitated as yellow sulphide on addition of hydrogen sulphide to the ammoniacal solution (or the blowpipe test, p. 361, may be applied).

D *The precipitate is orange-coloured.*

ANTIMONY is present. Confirm this by laying a piece of platinum foil in a dish, putting on it a bit of zinc, pouring over it 5 or 6 c.c. of dilute hydrogen chloride, and adding a few drops of the original solution. If a black deposit is formed on the platinum, the presence of antimony is certain.

E *The precipitate is dark brown or black.*

MERCURY, LEAD, COPPER¹, BISMUTH, TIN (as protosalt), GOLD, or PLATINUM is present.

Add to the liquid in which the precipitate is suspended, excess of solution of potassium hydrate (see note on p. 507), and heat the mixture.

(a) *The precipitate is dissolved.*

TIN, as a protosalt, is present (or possibly GOLD or PLATINUM).

In confirmation, add a drop of the original solution to some solution of mercury perchloride, which latter will be reduced to protochloride and form a white precipitate.

[It is not very likely that gold and platinum will be met with; but if tin is not detected by the above tests, separate portions of the original solution should be tested (a) for GOLD, with solution of iron protosulphate (p. 391), (b) for PLATINUM, with solution of ammonium chloride (p. 393).]

¹ If the solution has a blue or green colour, copper may be at once tested for as directed in 19'B.

(β) *The precipitate does not dissolve.* Pass on to the next paragraph.

19 Tests for mercury, copper, lead, and bismuth. The remaining metals must be successively tested for, as follows.

A Place a clean slip of copper in a portion of the original solution, acidified, if necessary, with dilute hydrogen chloride. The formation of a gray metallic film on the copper proves that MERCURY is present (see 17 B β). The changes in colour of the precipitate produced by addition of successive portions of hydrogen sulphide to the original solution (see p. 506, note) will have also indicated the presence of mercury, and the result of heating the dry substance with sodium carbonate in an ignition tube (9 A α) will afford absolute certainty.

[If hydrogen nitrate or aqua regia has been used in dissolving the substance, mercury may have been present originally in the monovalent condition, as a protosalt, such as calomel; this would be oxidised to a persalt by the solvent (p. 340). Observe whether the body has the characteristics of calomel, such as insolubility in water, volatility *without* fusion, &c.]

B Add to a portion of the original solution ammonia in excess.

(a) *A precipitate is at first formed which readily dissolves in excess of ammonia, forming a deep blue solution.*

COPPER is present. To remove any doubt, test another portion of the original solution with solution of potassium ferrocyanide, which should give a reddish brown precipitate of copper ferrocyanide.

(β) *A white precipitate is produced which does not dissolve in excess of the ammonia.*

LEAD or BISMUTH is present.

To distinguish between them, pour off a portion of the liquid in which the precipitate is suspended into another tube, and add at least an equal volume of dilute hydrogen sulphate.

If a white residue remains insoluble, LEAD is present. The reduction of the substance on charcoal before the blowpipe, (10) (*malleable globule, yellow incrustation*), will serve as a confirmatory test.

If the precipitate dissolves, BISMUTH is present. To confirm this, add to the rest of the liquid (containing the precipitate

formed by ammonia dilute hydrogen chloride, drop by drop, until the precipitate is just redissolved; then fill up the test-tube with water. *If the fluid becomes milky*, the presence of BISMUTH is confirmed. As a further proof, a portion of the original substance may be mixed with some sodium carbonate and reduced on charcoal before the blowpipe (*brittle globule, yellow incrustation*).

3. Examination for the Metals included in Group III.

IRON, COBALT, NICKEL, MANGANESE, CHROMIUM, ALUMINIUM, ZINC.

- 20** Ammonium sulphide test. Add to a portion of the original solution (1) one-fourth its volume of solution of ammonium chloride¹, (2) solution of ammonia until the liquid smells of it strongly, and lastly (3), whether ammonia has produced any precipitate or not, add three or four drops of solution of ammonium sulphide, and warm the mixture.

A No precipitate is produced.

None of the metals included in Group III are present. Pass on to 22.

B A black precipitate is produced.

IRON, NICKEL, OR COBALT is present.

[Before applying the next test, consider whether the original substance (or the residue from the original solution) became charred when heated in a tube (8B). Some organic substances, *e.g.* tartrates, citrates, sugar, prevent the precipitation of the hydrates by potassium hydrate. If, therefore, an organic substance is present, it will be safest to filter and wash the precipitate produced by ammonium sulphide, and then to dissolve it in hydrogen chloride (adding, if necessary, but not otherwise, a little hydrogen nitrate), and boil until all hydrogen sulphide is expelled. This solution should then be used instead of the original solution for the following test.]

Add to a portion of the original solution some solution of potassium hydrate.

¹ The ammonium chloride is added to prevent the possible precipitation of magnesium as hydrate by the ammonia.

- (a) *A dull green precipitate is formed, which becomes nearly black and finally reddish brown when shaken up for a short time in the tube, in order to expose it to the air.*

An IRON protosalt is present. In confirmation, test another portion of the original solution with solution of potassium ferricyanide, which should produce a deep blue precipitate (p. 402, expt. 5).

- (B) *A light green precipitate is produced, which does not alter in colour when exposed to the air or when the solution is boiled.*

NICKEL is present. The colour imparted to a borax bead by a portion of the substance will be the best confirmatory test (9 B 6, p. 494).

- (γ) *A light blue precipitate is formed, which slowly turns green in the air, and becomes reddish brown when the solution is boiled.*

COBALT is present. The blue colour imparted to a borax bead by a little of the substance will afford absolute certainty (9 B a, p. 493).

- (δ) *A reddish brown precipitate is formed.*

An IRON persalt is present. If so, hydrogen sulphide will have produced a precipitate of sulphur (18 B). Confirm this by testing another portion of the original solution with solution of potassium ferrocyanide, which will produce a deep blue precipitate of Prussian blue.

C *A precipitate is produced which is white, green, or gray (not black).*

The absence of iron, nickel, and cobalt is certain; it will be safest to test for all the other metals in this group.

[Before applying the next test, consider whether the original substance (or the residue from the original solution) *became charred* when heated in a tube (8 E). If it did, read the preliminary remark in the last paragraph (B) and proceed as there directed.]

Add to a portion of the original solution, some solution of potassium hydrate, drop by drop, observing whether a precipitate is produced, and if so, whether it dissolves in excess.

- (a) *No precipitate is produced.*

If the original solution is red or yellow, and nearly lost its colour when the ammonium sulphide was added just now, a CHROMATE

is present. This will be confirmed in the usual course of testing for acids (Sect. IV). Pass on to 22.

If the original solution was colourless, there is reason to test for a SILICATE, if this has not been already done, as directed in 16 B, p. 502.

- (β) *A gray precipitate is produced, insoluble in excess, and turning brown when shaken up with air.*

MANGANESE is present. To confirm this, heat some of the original substance in a borax bead (9 B, p. 493).

- (γ) *A dull bluish green precipitate is produced, soluble in excess, forming a green solution.*

CHROMIUM is present. The colour imparted to a borax bead (9 B, p. 493) will confirm this.

- (δ) *A white precipitate is produced, soluble in excess.*

ZINC or ALUMINIUM is present.

To distinguish between them, pour off some of the solution (containing excess of potassium hydrate) into another tube and add solution of hydrogen sulphide.

(αα) If this produces a white precipitate, ZINC is present. This should be confirmed by application of the blowpipe test, 10 A (*incrustation on charcoal, yellow while hot, white when cold; turning green on ignition with cobalt nitrate*).

(ββ) If no precipitate is formed, ALUMINIUM is present. To confirm this add some of the remainder of the solution (in potassium hydrate) to some solution of ammonium chloride in another test tube, and warm the mixture. The formation of a white gelatinous precipitate will confirm the presence of ALUMINIUM (but see note ¹).

- (ε) *A white precipitate is produced, insoluble in excess of potash, unaltered in air.*

The substance is an OXALATE, PHOSPHATE, FLUORIDE, or BORATE; the other radicle being BARIUM, STRONTIUM, CALCIUM, or MAGNESIUM². If so, it will have been found

¹ Solution of potassium hydrate often contains a silicate and aluminate, and a slight precipitate due to these must be allowed for. The best plan is to make the same experiment with the plain solution of potassium hydrate, and see if there is any difference in the amount of precipitate in the two cases.

² These salts are soluble in acids, but are reprecipitated, unaltered in composition, when the solution is neutralised. Hence either they must be examined by tests which can be applied to acid solutions, or they must be decomposed by other means.

soluble in hydrogen chloride, not in water? Pass on to the next paragraph.

- 21** Tests for Add to a portion of the original (acid) solution, &c., as tion, an equal volume of solution of calcium oxalate, &c. sulphate.

A An immediate white precipitate is formed.

BARIUM is present. The green colour imparted to flame (11) will serve to confirm this.

B A precipitate is produced, but only after the lapse of three or four minutes.

STRONTIUM is present. The crimson colour imparted to flame (11) will serve to confirm this.

C No precipitate is produced even after the lapse of eight or ten minutes.

Add to a portion of the original solution a few drops of dilute hydrogen sulphate and then 5 or 6 c.c. of alcohol.

If a white precipitate is formed, CALCIUM is present. The orange-red colour imparted to flame (11), for which the precipitate just obtained may be filtered off and used, will serve to confirm this.

If no precipitate is formed, MAGNESIUM must be present. To obtain positive evidence some of the original substance must be decomposed in the following way.

Boil some of the original substance (or solution) with 10 or 12 c. c. of solution of sodium carbonate for a couple of minutes, adding some solid sodium carbonate to saturate the solution. Filter, and wash the precipitate, which, if magnesium is present, will contain it as carbonate. Pour on the filter 2 or 3 c.c. of dilute hydrogen chloride, receiving the filtrate in a test-tube and pouring it again on the filter so as to dissolve the whole of the precipitate. Add to the solution (which will contain any magnesium present as chloride) about one-fourth its volume of solution of ammonium chloride, and then enough ammonia to make the liquid smell strongly of it; this will probably produce a precipitate, consisting of some undecomposed magnesium salt, which must be separated by boiling and filtering the liquid. Add to the clear filtrate a drop or two of solution of sodium-hydrogen phosphate, and shake the mixture. If a white granular precipitate is formed, MAGNESIUM is present.

Having found the metal you may proceed at once to test for an oxalate, phosphate, borate, and fluoride as directed in 30, &c., p. 521.

4. Examination for the Metals included in Group IV.¹

BARIUM, STRONTIUM, CALCIUM.

22 Ammonium carbonate test. To the portion of the solution in which ammonium sulphide has produced no precipitate, and which must also contain ammonium chloride and ammonia, add a few drops of solution of ammonium carbonate, and apply heat.

A *No precipitate is formed.*

None of the metals included in Group IV are present. Pass on to 23.

B *A white precipitate is formed.*

BARIUM, STRONTIUM, or CALCIUM is present.

Add to a fresh portion of the original solution an equal volume of solution of calcium sulphate.

(a) *A white precipitate is produced immediately.*

BARIUM is present. As a confirmatory test, add to another portion of the solution (neutralised if necessary) some solution of potassium chromate, which will produce a yellow precipitate if barium is present. Observe also the colour imparted by the original substance to flame (11).

(β) *No immediate precipitate is formed.*

STRONTIUM or CALCIUM is present.

Allow the solution to stand for four or five minutes, and then, if no turbidity appears, warm it.

(γ) *A precipitate is formed after the lapse of some time.*

STRONTIUM is present. The carmine-red colour imparted to flame (11) will be a conclusive proof.

(δ) *No precipitate is formed, even after the solution has been allowed to stand and warmed.*

CALCIUM is present. In confirmation, add to a fresh portion of the original solution enough ammonia to render it alkaline, and then a drop of solution of ammonium oxalate, which should produce a white precipitate¹. Observe also if the

¹ It must be borne in mind that this result is only characteristic of the presence of a calcium salt when barium and strontium have been proved to

substance imparts to flame a brick-red colour, which appears greenish gray when looked at through a piece of blue glass (11).

5. Examination for the Metal included in Group V.

MAGNESIUM.

23 Sodium-hydro- To the portion of the solution in which am-
gen phosphate monium carbonate produced no precipitate, and
test. which also contains other ammonium salts, add
a drop of solution of sodium-hydrogen phosphate, and, if
no precipitate is produced, rub the sides of the tube gently with
a glass rod.

A *No precipitate is formed.*

MAGNESIUM is absent. Pass on to 24.

B *A crystalline precipitate is formed.*

MAGNESIUM is present. In confirmation, ignite some of the
original substance on charcoal, moisten the white residue with
a drop of cobalt nitrate, and again ignite strongly. If the
mass is light pink when cool, the presence of magnesium is
confirmed (p. 452).

6. Examination for the Metals included in Group VI.

POTASSIUM, SODIUM, AMMONIUM, HYDROGEN.

24 To a fresh portion of the original solution placed in a small
beaker, add a little powdered calcium hydrate or oxide,
cover the beaker with a watch-glass on the under surface of
which a slip of moist reddened litmus-paper has been placed
(p. 465), and warm the mixture very gently for half a minute.

A *The litmus-paper is turned blue.*

AMMONIUM is present. In confirmation, observe the odour
of the gas, and see whether white fumes are formed when a
glass rod dipped in hydrogen chloride (or acetate) is held
within the beaker. The original substance will also have been
found, in part, at least, volatile when heated (8).

be absent: since either of the latter would, if present, yield a similar
precipitate.

B *The litmus-paper is unaltered.*

POTASSIUM, SODIUM, or HYDROGEN is present.

Add to another portion of the original solution, rendered slightly acid, if necessary, by hydrogen chloride, a drop or two of solution of **platinum perchloride**, and, if no precipitate is formed, evaporate the solution to dryness in a watch-glass and treat the residue with dilute alcohol (p. 456).

(a) *A yellow crystalline precipitate, or insoluble residue, is obtained.*

POTASSIUM is present. To remove any doubt, add to another portion of the solution (concentrated, if necessary) an equal volume of common alcohol, and test it with solution of sodium-hydrogen tartrate, which should produce a *white crystalline precipitate* (p. 457). Also observe if the substance imparts a lavender colour to flame, appearing crimson when looked at through blue glass (p. 457).

(β) *No precipitate or insoluble residue is obtained.*

SODIUM or HYDROGEN is present.

To test for the former metal, place a little of the original substance in a loop of perfectly clean platinum wire, and hold it in the flame of a Bunsen's burner. If an intense yellow colour, lasting for some time, is imparted to the flame, which is nearly or quite invisible when looked at through a piece of blue glass, the substance is a SODIUM salt.

[It must be remembered that mere traces of sodium (which is nearly always present as an impurity in other substances) will colour the flame yellow. But such traces are soon volatilised, and hence if the substance continues for some minutes to impart an intense yellow colour to the flame, it may be certainly inferred to be a sodium salt.]

If sodium is not found, and no other metal has been detected in the previous stages of the analysis, the basic radicle is probably HYDROGEN alone.

The presence of a hydrogen salt will have been already inferred in the preliminary examination (15 B). Proceed with the examination for the other radicle (Sect. IV); and when it is found, consider whether the original substance possesses the properties, such as volatility, of its hydrogen salt.

SECTION IV.

EXAMINATION OF A SINGLE SUBSTANCE FOR A
NON-METALLIC RADICLE.

Consider, in the first place, what radicles may be inferred to be present from the solubility or insolubility of the substance in water, and the results of the preliminary examination.

(a) If it is soluble in water, the radicle sought must be one of those which form compounds soluble in water with the metal which is known to be present.

(b) If it is insoluble in water, but soluble in acids, the radicle must be one of those which form compounds soluble in acids only, with the metal which is known to be present.

The Table in Appendix E will serve as a guide, but there are so many degrees of solubility that it is not always safe to infer the presence or absence of a radicle on this ground alone.

The following radicles will have been detected with certainty in the preliminary examination, and will not be further referred to in the course.

CARBONATE (8 F γ , 12 A).	NITRITE (12 H).
SULPHIDE (12 F).	SILICATE (4 B β , 16 A, B).
SULPHITE (12 D).	HYPOCHLORITE (12 G).
THIOSULPHATE (8 D ζ , 12 D).	HYPOPHOSPHITE (8 F δ).
CYANIDE (8 F β , 12 C).	

1. Examination for TARTRATES, ACETATES, CHROMATES, SULPHATES, and FLUOSILICATES.

25 Refer to the results obtained by heating some of the original substance (or the residue obtained by evaporating the solution) in an ignition tube (8).

A The substance became charred.

It is a TARTRATE, or ACETATE (or possibly an OXALATE¹).

Boil some of the original substance with some solution of sodium carbonate; or, if it was a liquid, add excess of sodium carbonate to it; filter, if necessary, and add a few drops of solution of silver nitrate to the clear liquid, sufficient to produce a white precipitate of silver carbonate; lastly, boil it for half a minute, adding more silver nitrate if the precipitate dissolves.

(a) *The precipitate turns black.*

The substance is a TARTRATE.

(β) *The precipitate remains unaltered in colour, or only turns light brown.*

The substance is an ACETATE (or OXALATE).

To make sure whether an acetate is present or not, acidify a little of the original solution (if not already acid) with hydrogen chloride, add a little powdered chalk or marble, boil, and filter (the reaction is explained in expt. 4, p. 215). To the clear filtrate add one drop or less (on a glass rod) of solution of iron perchloride. If the solution turns red and, when boiled, gives gradually a reddish-brown precipitate, an ACETATE is present.

If it is not found, test for an oxalate as directed in 30.

[CITRATES, though not of very common occurrence, may be here examined for, if an acetate is not found, before passing on to 30. Add to some of the original solution about 1 c.c. of solution of ammonium chloride, then enough ammonia to render it alkaline, and lastly some solution of calcium chloride.

If a precipitate forms at once, an OXALATE is present. Pass on to 30.

If no precipitate is formed, boil the liquid for half a minute. If a crystalline precipitate gradually forms, a CITRATE is present.]

B The substance did not become charred. Pass on to the next paragraph.

26 Barium chloride test. Add to a portion of the original solution (which, if acid, must be made slightly alkaline by ammonia: any precipitate thus formed being filtered off)

¹ These (unless quite pure) become, in many cases, more or less charred when heated.

a few drops of solution of **barium chloride** ¹ or **barium nitrate**, if lead, silver, or mercury as protosalt is present ¹).

A No precipitate is formed. Pass on to 27.

B A yellow precipitate is formed.

The substance is a **CHROMATE**. This will have been suspected already (18 B, 20 C a), and may be confirmed by the colour imparted to a borax bead (green in both flames).

C A white precipitate is formed.

This may indicate the presence of any of the radicles included in Group I (p. 479).

Add to this an excess of dilute **hydrogen nitrate**.

(a) The precipitate dissolves. Pass on to 30.

(β) The precipitate remains undissolved.

A **SULPHATE** is present.

Confirm by testing the original solution (which must not contain hydrogen chloride), acidified with hydrogen nitrate, with solution of **lead acetate**, which will cause a white precipitate if a sulphate is present ².

[**FLUOSILICATES** also give a precipitate with barium chloride, insoluble in acids. Hence if no precipitate is obtained with lead acetate, it will be well to test the substance for a fluoride as directed in 88, p. 523, and, if it is present, to place over the leaden cup a slip of glass on the under side of which a drop of water has been deposited. If a white film is formed in and around this, silicon fluoride is being evolved as well as hydrogen fluoride, and the substance is a fluosilicate.]

2. Examination for **BROMIDES, IODIDES, FERRO-CYANIDES, THIOCYANATES, CHLORIDES, and CYANIDES.**

27 **Silver nitrate** Add to some of the original solution (which test. must have been made with water or hydrogen nitrate, *not* hydrogen chloride) enough concentrated **hydrogen**

¹ A little barium nitrate for this purpose may be readily prepared by dissolving a small quantity of barium oxide, hydrate, or carbonate, in dilute hydrogen nitrate.

² Another very good confirmatory test for a sulphate is, to fuse the substance on charcoal with a little **sodium carbonate** (see p. 289), and examine the fused mass for a sulphide.

nitrate (at least one-sixth its volume) to render it *strongly*¹ acid, and test it with solution of silver nitrate.

A *No precipitate is formed.* Pass on to 28.

B *A white or light yellow precipitate is formed.*

The solution contains one of the above-mentioned radicles.

Add to some of the original solution, acidified with hydrogen nitrate, a few drops of solution of chlorine.

(a) *The liquid turns yellow.*

A BROMIDE or IODIDE is present.

Pour off some of the yellow solution into another tube and add some freshly-made solution of starch.

If the liquid turns deep blue, an IODIDE is present.

If the liquid does not change colour, a BROMIDE is present. Confirm by adding to the remainder of the yellow liquid (to which more chlorine may be added) some carbon disulphide, and shaking it up. If the globule which sinks to the bottom is orange-coloured, the original substance is a BROMIDE.

(β) *The liquid does not turn yellow.*

A FERROCYANIDE, THIOCYANATE, CHLORIDE, or CYANIDE is present.

Test a portion of the original solution (acidified with hydrogen chloride, if not already acid) with solution of iron perchloride. If this produces a blue precipitate, a FERROCYANIDE is present.

If the liquid turns deep red, a THIOCYANATE is present.

If no alteration takes place, the substance is a CHLORIDE, or CYANIDE (the latter should have been detected already in 12). To ascertain if a chloride is present, put some of the original substance, or solution (in water or hydrogen nitrate), into a test-tube, add a little manganese dioxide and then 2 or 3 c.c. of strong hydrogen sulphate, and warm it gently.

If a greenish yellow gas, which bleaches moist litmus-paper, is given off, the substance is a CHLORIDE.

[A hypochlorite would give a similar reaction but this radicle, if present, should have been detected already in 12 G, p. 499.]

If a chloride is not found, a CYANIDE should be tested for, if this has not already been done, as directed in 12.

¹ If the solution is only slightly acidified, an oxalate may, if present, cause the formation of a precipitate of silver oxalate.

3. Examination for CHLORATES, NITRATES, OXALATES, PHOSPHATES, BORATES, and FLUORIDES.

These radicles should be tested for in separate portions of the original substance or solution, in the following order:—

- 28** Test for chlorates. Add a drop of indigo sulphate to a little dilute hydrogen sulphate in a test-tube; add to this a few drops of solution of hydrogen sulphite (or a small crystal of sodium sulphite); then add a few drops of the original solution to be tested¹.

If the blue colour of the indigo disappears at once without heating, a CHLORATE is present. Confirmatory evidence of this will be found in 8 F γ (evolution of oxygen on heating) and 12 G (evolution of chlorine tetroxide).

If the indigo remains unaltered (for a time, at all events), pass on to the next paragraph.

- 29** Test for nitrates. Add to some of the original substance (or of the concentrated solution) a little strong hydrogen sulphate, shake up, and cool the mixture in a stream of water. When it is quite cold, hold the tube in a slanting position, and pour slowly down the side a little solution of iron protosulphate, so as to form a layer on the top of the denser acid solution: then allow it to stand for a minute.

If a dark brown layer is formed (either immediately or in the course of a minute or two) where the two liquids are in contact, which disappears when the whole is shaken up and heated, orange vapours appearing in the tube, a NITRATE is present. If not, pass on to the next paragraph.

- 30** Test for oxalates. Put a little manganese dioxide into a test-tube, add a few drops of water and about twice as much strong hydrogen sulphate. [If any effervescence occurs, wait until it has ceased.] Then add a little of the original substance, or the strong solution.

¹ If lead, barium, or strontium is present, a precipitate will, of course, be formed; but this may be neglected.

If an *effervescence begins*¹ (best observed by the hissing sound when the open end of the tube is held to the ear), and if the gas given off is found to be carbon dioxide by the limewater test (p. 195), the substance is an **OXALATE**. If not, pass on to the next paragraph.

- 31** **Test for** Place some solution of **ammonium molyb-**
 phosphates. **date** in a tube, add a few drops of the original
 solution (acidified, if necessary, with hydrogen nitrate) and
 warm it gently (but do not boil it).

*If a yellow precipitate is formed, a PHOSPHATE is present*².

[An arsenate would give a similar reaction. If arsenic has been found in the reduction in an ignition-tube (9 A β, p. 493), boil some of the original solution (neutralised, if necessary, with ammonia) with a small crystal of sodium thiosulphate: then add excess of hydrogen chloride and boil again. *If a yellow precipitate is produced* (of arsenic sulphide) an arsenate is present. *If only a white milky precipitate* of sulphur forms, the substance is a phosphate.]

If this is not found, pass on to the next paragraph.

- 32** **Test for** Place a little of the substance, or of the con-
 borates. centrated solution, in a watch-glass, add sufficient
 dilute hydrogen chloride to make the mixture decidedly acid
 (if it is already acid, this need not, of course, be done), dip into
 the liquid one-half of a strip of turmeric paper, and dry it by
 holding it on wire-gauze at some distance above a small lamp-
 flame.

If the dipped portion becomes faintly red, and turns bluish black when a drop of solution of sodium carbonate is placed upon it, a BORATE is present. To obtain further proof, put a little of the substance (or solution) into a small dish, add some alcohol and several drops of strong hydrogen sulphate; stir them together, and set fire to the mixture. *If a borate is present, the flame will be edged with green.*

¹ Carbonates, tartrates, and citrates must have been previously proved to be absent.

² This test, of course, applies strictly to orthophosphates, which are the only phosphates of common occurrence. For the distinctive tests for pyro- and metaphosphates, see p. 223.

- 33** Test for fluorides. Put some of the original substance (or of the residue obtained by evaporating the solution) into a capsule of lead or platinum; add a few drops of strong hydrogen sulphate, and stir the whole together. Cover the capsule with a glass plate coated with wax (see p. 265), and having some letters traced on it, as there directed; and place the capsule on some warm sand for four or five minutes.

If, on removing the wax, the letters are permanently etched into the glass, the substance is a FLUORIDE.

If no non-metallic radicle can be detected by the above course of examination, the substance may be an oxide. Observe whether it has the characteristic properties of the oxide of the metal which has already been found.

4. Methods of separating the metal in special cases.

- 34** Separation of the metal. If the above tests have given no satisfactory results, it will be advisable to separate the metal and to obtain the other radicle in combination with sodium or ammonium. The means to be employed for effecting this will depend upon the metal present.

A The metallic radicle belongs to Group I, II, or III.

Boil some of the substance or solution with 5 or 6 c.c. of solution of ammonium sulphide for a few minutes¹: allow any residue to subside, decant the clear solution into a porcelain dish, and evaporate it to dryness. Warm the residue with some water, filter the solution, which (unless the original substance was an ARSENIC, ANTIMONY, or TIN salt) will contain only the non-metallic radicle associated with ammonium, and examine it as directed in 12 and 25.

[If ARSENIC, ANTIMONY, or TIN have been found to be present the solution will contain ammonium thioarsenate, thioantimonate, or thiostannate. In this case, add to the solution a slight excess

¹ If the metal belongs to Group I or II, it may be separated by adding excess of solution of hydrogen sulphide to some of the original solution; or, to avoid the great dilution thus caused, a current of hydrogen sulphide gas may be passed through some of the solution in a test-tube or small flask. The non-metallic radicle is thus obtained in solution as a hydrogen salt.

of dilute hydrogen nitrate, which will throw down the metal as sulphide, filter the solution, and examine it as directed in 12 and 25, remembering that a NITRATE is now present.]

B The metallic radicle belongs to Group IV or V.

Boil some of the substance with solution of sodium carbonate for a few minutes, filter the solution, and test it as directed in 12 and 25, decomposing the excess of sodium carbonate with dilute hydrogen chloride or nitrate, as required.

SECTION V.

ANALYSIS OF A SINGLE SUBSTANCE WHICH IS
INSOLUBLE IN WATER AND ACIDS.

It will be seen, by a reference to the Table of Solubilities (Appendix E), that the salt must be one of a very limited number of substances. The following list includes all the insoluble substances which are commonly met with in inorganic analysis:—

(LEAD SULPHATE).	(ALUMINIUM SESQUIOXIDE).
SILVER CHLORIDE.	BARIUM SULPHATE.
SILVER BROMIDE.	STRONTIUM SULPHATE.
SILVER IODIDE.	(CALCIUM FLUORIDE).
TIN DIOXIDE.	ALUMINIUM-SODIUM FLUORIDE
(ANTIMONY TRIOXIDE).	(cryolite).
(ANTIMONY PENTOXIDE).	BARIUM FLUOSILICATE.
IRON FERROCYANIDE (Prussian blue).	SILICON DIOXIDE.
CHROMIUM-IRON OXIDE	SILICATES of various kinds.
(chrome iron stone).	SULPHUR.
(CHROMIUM SESQUIOXIDE).	CARBON.

[The substances enclosed in brackets dissolve with great difficulty in acids.]

SULPHUR will have been recognised already (8 D §).

35 Action of potassium hydrate. Boil some of the substance with strong solution of potassium hydrate.

A No action takes place. Pass on to 36.

B The substance is decomposed or dissolved.

Add water, and filter if necessary. Examine the filtrate by the usual course for a non-metallic radicle, beginning at 13 and 25. Wash the residue, if any; dissolve it in hydrogen nitrate, and examine the solution for a metal, beginning at 17.

36 Refer to the results obtained by heating the substance in an ignition tube (8).

A The substance was unaltered, and is dark-coloured. It may be chromium-iron oxide (chrome iron stone), chromium sesquioxide, carbon, or one of certain silicates.

Powder a little of it and mix it intimately with about twice as much potassium nitrate; put some of the mixture into an ignition-tube and heat it, at first gently, afterwards as strongly as possible.

(a) *The substance deflagrates.*

It is CARBON (charcoal or graphite; if the latter, it will have been acted on only with difficulty, and will have a metallic lustre). To confirm this, dip the bulb, while hot, into a very little water in a dish, when it will crack off; pour off the solution into a test-tube and examine it for a carbonate as directed on p. 195.

(β) *The substance is acted on with formation of a yellow mass.*

It is CHROMIUM-IRON OXIDE, or CHROMIUM SESQUIOXIDE (if the latter, it will be green). Detach the yellow mass by dipping the hot bulb into water, as directed just above; powder it, and boil it with water; then filter it and examine the filtrate for a chromate as directed in 26. If any brown residue remains on the filter, it is probably iron oxide, and should be dissolved in a little hydrogen chloride, and the solution tested for iron with potassium ferrocyanide.

(γ) *No action occurs.*

The substance is probably a SILICATE. Pass on to 37.

B The substance was unaltered, or only fused, and is white or light yellow.

Mix a little of it with potassium cyanide, and heat it strongly on charcoal, as directed in 10, if this has not been done already.

(a) *A metallic globule is obtained.* The substance is one of the above compounds of SILVER, LEAD, TIN, or ANTIMONY.

Refer to 10 B to decide which metal is present from the character of the globule and incrustation; and, if there is any doubt, treat the globule with hydrogen nitrate as directed in 7, p. 488.

If LEAD is found, boil some of the original substance with solution of sodium carbonate, and test the solution for a sulphate.

If SILVER is found, mix a little of the original substance with about three times as much sodium carbonate, and fuse the mixture in an ignition tube, or on a bit of porcelain: powder the fused mass and boil it with water, filter, and examine the filtrate for a bromide, iodide, and chloride as directed in 27 B.

(β) *No metallic globule is obtained.*

In this case it will be best to decompose the substance by fusion with sodium carbonate, as directed in the next paragraph.

37

Fusion with
sodium car-
bonate.

Reduce some of the substance to an impalpable powder (using an agate mortar, if possible), and mix it with about four times its weight of sodium carbonate (or of a mixture of sodium carbonate with potassium carbonate, which fuses at a much lower temperature than sodium carbonate alone). Place the mixture in a platinum capsule¹ or on a piece of platinum foil turned up at the edges (p. 8), and heat it strongly over the gas blowpipe (or in a small gas furnace, if at hand), until all action is over and the mass is in a state of calm fusion. After allowing it to cool, detach it from the capsule, and grind it with a little water in a mortar; then transfer the whole to a beaker, and boil it for a few minutes with about 20 c.c. of water.

[While this is going on, a fluoride may be tested for by heating a little of the substance (in a platinum vessel) with strong hydrogen sulphate, and observing whether vapours are evolved which etch glass (p. 265). If a fluoride is found to be present, continue heating the substance with hydrogen sulphate for five or six minutes, then allow the mass to cool, add a little water, mixing it thoroughly with the substance, and boil the mixture in a test-tube. Test the filtered solution for aluminium (20 C) and calcium (22 B δ).]

By this treatment* the metals are separated as insoluble

¹ An iron cup will do; but if this is used, iron must be tested for in a separate portion of the substance.

carbonates or oxides, while the non-metallic radicals are obtained in solution as sodium salts.

Pour the whole on a filter, and test the filtrate (which, of course, contains excess of sodium carbonate) by the usual course for a silicate, sulphate, and fluoride.

Wash the residue, dissolve it in dilute hydrogen chloride (pouring the warm acid several times over it, on the filter), and test it for a metal by the usual course.

SECTION VI.

EXAMPLE OF THE ANALYSIS OF A SINGLE
SUBSTANCE.

The following account is intended as an illustration of the proper scientific way in which the course of examination of an unknown substance should be written out, in accordance with the principles given on p. 481.

(The substance taken was manganese chloride.)

The single substance for examination was a light pink solid, not crystalline, which soon became moist when exposed to the air, and was readily powdered in a mortar.

A. Preliminary Examination.

1. A portion of the substance, heated in a test-tube with some water, readily dissolved, forming a nearly colourless solution which was neutral to test-paper.

2. A little of the solid substance was heated gently in an ignition-tube. It gave off traces of water, and when heated nearly to redness it fused into a brownish liquid which solidified, on cooling, into a pink crystalline mass. No vapours were given off, and no charring of the substance was observed.

Hence no organic radicle is present.

3. Since the substance was coloured, a little of it was heated in a borax bead before the blowpipe. It gave a transparent bead which was amethyst-red in the oxidising flame and colourless in the reducing flame.

Therefore manganese is present.

4. A little of the substance was gently warmed with strong hydrogen sulphate in a test-tube. It gave off pungent colourless vapours, which reddened litmus-paper, but had no very characteristic smell or action on the glass.

B. Examination of the Solution for a Metal.

1. A portion of the solution was tested with a few drops of dilute hydrogen chloride.

No ppte. was formed.

Therefore silver, mercury (as protosalt), and probably lead, are absent.

2. To the same portion of the solution (containing hydrogen chloride) was added an excess of solution of hydrogen sulphide, and the mixture was warmed.

No ppte. was obtained.

Therefore no metal belonging to Group II is present.

3. Another portion of the original solution was mixed with some solution of ammonium chloride, rendered alkaline with ammonium hydrate (which caused a ppte.), and tested with a drop of solution of ammonium sulphide.

A ppte. was formed, which was dull pink, not black, in colour.

Therefore the metal belongs to Group III, but is not iron, cobalt, or nickel.

4. Some of the original solution was tested with potassium hydrate.

A gray ppte. was formed, which became brown on being shaken up.

Therefore the metal present is Manganese.

This was confirmed by the colour imparted to the borax bead.

C. Examination for the non-metallie Radicle.

Since the substance is a manganese salt readily soluble in water, the following radicles may be present:—Nitrate, Acetate, Chloride, Iodide, Bromide, Sulphate, Chromate.

It is not an acetate, since it did not blacken when strongly heated.

It is not a chromate, since the solution was nearly colourless, and gave no ppt. of sulphur when warmed with hydrogen sulphide.

It is probably not a nitrate, since no perceptible decomposition took place when it was heated.

1. A portion of the original solution was tested with a drop of solution of barium chloride.

A slight turbidity was produced, which did not disappear when excess of hydrogen nitrate was added; but as the ppt. was quite disproportionate to the quantity of salt known to be in solution, it proved that a sulphate was present only as an impurity.

2. Another portion of the original solution was acidified with hydrogen nitrate and tested with solution of silver nitrate.

A white flocculent ppt. was formed.

Therefore the substance is an iodide, bromide, or chloride.

3. Some of the original solution was acidified with hydrogen nitrate and tested with solution of chlorinc.

No yellow colour appeared.

Therefore the substance is not an iodide or bromide, but probably a chloride.

To confirm this a little of the solid substance was mixed with some manganese dioxide, and warmed in a test-tube with some strong hydrogen sulphate. A gas was given off which was proved to be chlorine by its odour, its yellowish green colour, and its bleaching action on a piece of litmus-paper held in the tube.

Therefore the non-metallic radicle is Chlorine.

And the substance is Manganese Chloride.

APPENDIX A.

SUGGESTIONS FOR THE CONSTRUCTION OF
CHEMICAL APPARATUS.

THE set of apparatus described at the beginning of this book is, necessarily, a rather expensive one; and although it includes nothing which would not be found in a regular laboratory, yet a student who is working by himself may not find it possible or advisable to spend so much on the materials for his experiments.

The object of the present chapter is to supply a few hints for the construction of simpler and cheaper forms of apparatus, such as may be made by any one possessed of a little mechanical skill and a few carpenter's tools. The student should never rest satisfied with clumsy makeshifts; he should endeavour to do the best he can with the materials he has at hand.

[The numbers refer to those in the list of apparatus at the beginning of the book.]

2. Measures. A method of making these has been illustrated on p. 49. Larger measures than the one there mentioned can, of course, be made in the same way; a tall, narrow, wide-mouthed bottle or jar¹ being counterpoised in the balance, and 10, 20, &c. grms. of water weighed into it. Or, successive portions of 10 c.c. of water may be measured into the jar from the small test-tube measure already made. The graduation-marks may be either made with a file or, more neatly, by covering the whole of the outside of the jar with wax before graduating it, scratching the requisite marks and figures through the wax with a pointed bit of hard wood or of wire, and exposing it to the vapours of hydrogen fluoride prepared in the usual way (p. 265). A long narrow trough of sheet lead will serve to contain the fluor spar and acid. •




4. Weights. Duplicates of any of the smaller weights to which

¹ A common flower-vase may often be obtained which answers the purpose well.

you have access may be readily made out of strips of sheet brass or lead, cut at first decidedly heavier than the intended weight, and then carefully reduced, first by cutting off small strips with a pair of shears or scissors, and lastly by filing, until they exactly balance the standard weight.

When a strip has been cut off and the weight is still too heavy, you may ascertain whether it will be safe to cut off another similar strip by putting the piece cut off in the same scale as the standard weight, and observing whether the weight you are making is still too heavy; if it is, another strip equal in size to the last may be cut off. If the piece of metal is inadvertently made too light, it may still, of course, serve for a duplicate of the next smaller weight. Figures or marks showing its value should be scratched or punched upon the metal *before* it is quite reduced to the proper weight.

If no standard weights are at hand to be copied (but only in such a case), a set of small weights such as fractions of the gramme may be made as follows:—

Obtain a piece of rather thin brass wire about 12 or 15 cm. long (10 cm. of brass wire, No. 18 wire gauge, 1.22 mm. diameter, weigh almost exactly 1 gm.), and reduce it to the weight of 1 gm., by cutting off pieces as above directed. Then straighten it and cut it *exactly* in half (using cutting-pliers or scissors, not a file). This will give two pieces each weighing 5 decigrammes; keep one of these as a weight, bending it into a 5-sided figure, thus, , to indicate its value. Divide the other piece accurately into five equal parts. This may be done by drawing a line equal to it in length on a piece of paper, and stepping along this line with a pair of compasses; a few trials will give the proper length of one division, . Lay down the wire close to the line on the paper, and mark each division on it with ink; then cut it at the 1st and 3rd divisions. You have now a piece weighing 1 decigramme, and two others each weighing two decigrammes. Bend each of the two latter in the middle to a right angle, thus, , to indicate its value, but leave the 1 decigramme straight. You will then have all the necessary decigramme weights, 5, 2, 2, 1; and centigramme weights may be made in the same way, a piece of thinner wire being taken.

5. *Pneumatic Troughs.* An earthenware pan, a large biscuit tin, or even a wooden box (covered with three or four coats of good paint) will answer the purpose. The shelf may be made of a sheet of tin plate or zinc, about 12 or 14 cm. wide, and sufficiently

long to reach across the trough. A portion on each side about 1 cm. broad should be bent down, as shewn in fig. 98, to give stiffness to the shelf, and a hole about 2 cm. in diameter should be cut in the centre. The size of the hole should first be traced out with a pair of compasses, and the metal may then be cut with a chisel or with the blade of a strong knife struck with a hammer, the plate being laid on a piece of board. To suspend this shelf in its place in the trough the ends of the strip of tin should be turned up and bent over the rim of the trough. Or, four pieces of strong brass wire may be passed through holes made at the four corners of the shelf, and bent up over the rim. Instead of tin plate the shelf may be made of wood (well painted), having one or two pieces of lead nailed on its under side to sink it, and suspended by wire hooks.

Instead of a shelf reaching across the trough, a 'bee-hive' shelf, fig. 97, may be used. This is intended to stand on the bottom of the trough, the delivery tube being introduced into the side-

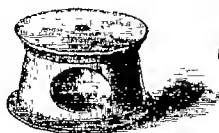



Fig. 97.



Fig. 98.

opening, and the gas jar being placed over the central aperture. Such a shelf may be purchased for a shilling, or less; but it may be easily made out of a common gallopot, or flower-pot saucer. The hole in the centre may be pierced by gradually chipping away the material with the point of an old three-square file, care being taken that the blows of the hammer are light. The notch at the side may be cut out by chipping or crumbling away the earthenware with a pair of pliers. There is, of course, some chance of breaking the pot, but if it is placed on a folded cloth, and if the chipping is carefully and patiently done, the risk is slight.

Finally, an extempore shelf may be made by placing two bricks side by side in the trough, a sufficient interval being left between them to admit the delivery tube.

6, 7. Supports for Flasks, Tubes, &c. A very useful tripod-stand for supporting sand-baths, &c., may be made by taking three pieces of stout iron wire or thin rod, about 45 cm. long, bending them into this form, , and binding them together by folds of thin iron wire, so as to form the stand represented in fig. 99.

For small crucibles, a triangle support is extremely useful, fig. 100. It is made by taking three bits of tobacco-pipe stem about 6 cm. in length, passing through each a piece of iron wire of such a length that about 4 cm. projects at each end of the pipe stem, and then twisting together these projecting pieces of wire.¹ It is intended to be laid on the ring of a retort-stand or on the tripod-stand above mentioned¹.

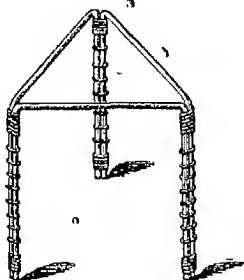


Fig. 99.

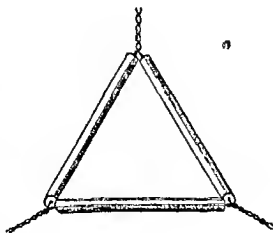


Fig. 100.

A simple form of holder is represented in fig. 101, next page, which may be constructed by the student himself. The base (12×24 cm.) and the upright (5×30 cm.) are made of deal about 2.5 cm. in thickness. The upright is mortised and glued into the base, and has a slit about 5 mm. wide cut in it to a distance of 20 cm. from the top. The arm *a* is of harder wood, such as birch or beech, and is 3 cm. square and 7 cm. long. The screw *b* is one of the common brass thumb-screws sold by ironmongers; a hole is bored in the arm *a* to receive it, and its nut is inserted in a small mortise cut in the arm about 2 cm. from the end. The screw passes through a collar (for which a small brass or iron pulley answers well) on the other side of the upright, and by tightening it the arm may be secured at any height. At the other end of the arm a saw-cut is made in which are placed two strips of stout tin or brass plate about 12×3 cm., firmly secured by the two screws shewn in the figure. The outer ends of these strips are curved so as to grasp a tube or a retort, and their grip is tightened by slipping outwards the ring *c*. This latter is a common curtain ring 2.5 cm. in diameter carefully flattened into the shape of an elongated ellipse.

8, 9. Gas-burners. It will be best to obtain at starting a fish-

¹ Such a triangle is also very useful for supporting a funnel, containing a filter, over a beaker. For this purpose a piece of thin board, about 6×12 cm., with a hole in the middle, will answer equally well.

tail burner attached to a firm base, such as is represented in fig. 6 (p. 6), since a blowpipe burner and a Bunsen's burner can be easily fitted to it.

A serviceable, though not ornamental, form of base is shewn in fig. 102. It consists of a block of wood, about 8 cm. square, of which is fixed, by means of two screws, a 'three-eighths angle

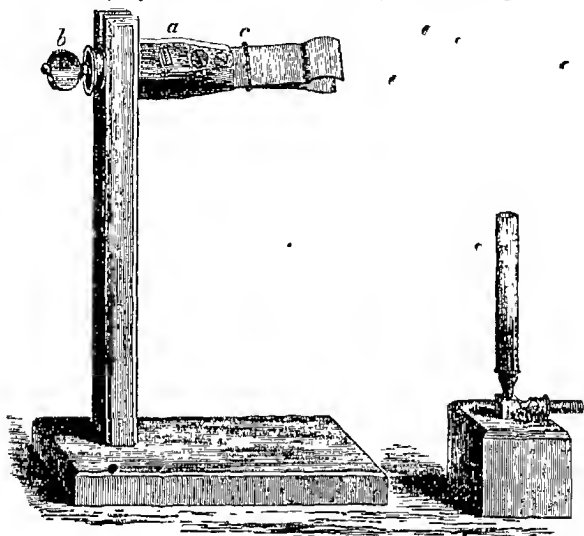


Fig. 101.

Fig. 102.

burner' with fish-tail nipple, which may be procured from any gas-fitter. A stop-cock need not necessarily be fitted to it, since the stop-cock of the supply pipe will regulate the current of gas.

A **Blowpipe Burner**, of the form of fig. 6 *b* (p. 6), may be made of a piece of brass tubing about 1 cm. in diameter and 5 cm. in length, having one extremity cut obliquely and flattened in a vice. The flattening should not be carried so far as to close the opening, but a narrow slit about 1 mm. in width should be left. This tube may then be fitted over the fish-tail nipple by an india-rubber connector.

A **Bunsen's Burner** may be made, as shewn in fig. 102, by placing over the fish-tail nipple a tube of glass or brass open at both ends, about 1.5 cm. in internal diameter and 12 or 14 cm. in length, secured in its right position by two wedges of cork or soft wood. Plenty of room should be left for air to enter at the lower

end, and the tube should be raised or lowered a little, until a non-luminous flame is obtained. A tube of brass is, of course, the best, but a piece of 'composition' (lead and tin) gas tubing will answer. Instead of leaving air-space at the bottom of the tube, it may be fitted close round the burner, and two large notches may be filed, one on each side, at such a height that, when the tube is fixed in its place, the top of the fish-tail jet may be 1 mm. below the highest part of the notch.

A test-tube, the closed extremity of which has been cut off, makes a very useful burner; the only drawback being that the flame is slightly coloured by the sodium of the glass, and that the top is likely to crack. This may be obviated by fitting over the top of the tube a short metallic ferrule, made by wrapping a strip of thin brass or tin plate, about 3 cm. broad, round a cylindrical rod a little smaller than the burner itself. The strip should be of such a length that its ends overlap each other, and the joint need not then be soldered. The elasticity of the metal will keep it in its place, when it is fitted over the end of the glass tube burner.

A still simpler form of burner may be made as follows. The gas-jet is formed by flattening one extremity of a short elbow tube, as in making the blowpipe burner, until a narrow slit remains. Over this is fitted a test-tube, as above described, by wedges of cork, and the elbow tube is fitted into a notch cut in a large cork. This latter is fitted over the beak of an inverted funnel which serves as the base.

A Ring-burner, which will serve the purpose of an Argand burner, is represented in fig. 103. It is nothing more than a flat, hollow, brass door- or cupboard-handle, about 4 cm. in diameter, round which eight or ten small nicks have been cut with a file, through which the gas issues. The hole into which the axis of the latch fitted should be enlarged with a rat-tail file and with a broach (for which latter the tapering end of a screw-driver will serve), until the cylindrical part of the fish-tail nipple will just enter it.



Fig. 103.

12. A Sand-bath may be made by turning up the edges of a piece of tin plate about 16 cm. square, so as to form a shallow tray 2 cm. in depth. The shallow tin 'pastry-pans' sold by ironmongers answer very well.

A Water-bath, which is often convenient and sometimes necessary for evaporations at a gentle heat, may be made of a saucepan

or a short tiff canister, in the lid of which a hole is cut rather smaller in diameter than the evaporating dish. A glue-pot makes an excellent water-bath. The bath should be about half filled with water, which must be kept gently boiling over a lamp; the dish containing the solution to be evaporated is placed in the opening of the lid, so as to be exposed to the heat of the steam.

A beaker will answer the purpose fairly, the dish being placed upon it, and slightly raised at one part by interposing a bit of wire or a splinter of wood, so as to allow free exit for the steam.

14. A Mouth Blowpipe, made of glass, is represented in fig. 104. A good sound cork is selected, a hole is bored two-thirds



Fig. 104

of the way through it, and another hole is then bored in the side to meet the first. Into this latter hole is fitted a short jet of difficultly-fusible glass tubing, and into the other hole is fitted a piece of glass tube about 20 cm. in length. A bulb may be blown on this latter tube near its lower end, to serve as a reservoir for condensing the moisture of the breath.

17. For a Cork-borer the tube of a steel pen-holder will answer pretty well, but it is hardly strong enough to last very long. Holes may be made in corks by means of the rat-tail file alone, the latter being worked into the cork like a gimlet. As, however, the file does not cut through, but pushes aside the particles of cork, there is some risk of splitting the cork.

21. A Deflagrating Cup may be made of the bowl of a tobacco-pipe, partly filled up with plaster of Paris (for the method of using this, see p. 448), in order to reduce its depth. A piece of copper wire should be twisted round the bowl, and the end bent up and passed through a large cork, or bung. Instead of a tobacco-pipe bowl, a small block of chalk or of plaster of Paris, hollowed into a cup, may be used.

22. A Deflagrating Jar, which answers the purpose well, may be made by cutting off the bottom of a large wide-mouthed glass bottle. This is best done by leading a crack round it by means of

a piece of heated glass (p. 43). The crack should be begun at the edge, the red-hot glass being pressed against it for a short time, and then a drop of water applied. There is generally some little difficulty in inducing the crack to follow the heated glass evenly, owing to the irregular thickness of the glass near the bottom of the bottle, and the crack should never be left to itself for any time, lest it should extend itself in a wrong direction. A bottle may often be found which is thinnest where it should be strongest, *viz.* at the angle formed by the sides and the bottom. In this case the bottom may generally be detached evenly by a sharp blow of an iron rod introduced through the neck of the bottle.

The edges of the glass should be roughened with a file, and it is advisable, though not necessary, to grind them level upon a flat paving stone with the assistance of a little fine sharp sand, or emery, and water. The jar should be rubbed on the stone with circular strokes, not backwards and forwards, or the edges are likely to chip away.

24. Very useful **Gas Jars** may also be made out of bottles; the necks being cut off in the manner above described. For most purposes, however, tall wide-mouthed bottles will answer without alteration. The small bottles, about 14×5 cm., in which quinine is sold, are particularly suitable for experiments; but gases should not be exploded in them.

26. Instead of the stoneware **Trays for Gas Jars**, common saucers may be used.

28. **Florence Flasks** will answer almost every purpose for which flasks are required. Their necks are rather narrow for a cork in which two tubes have to be fitted; the latter must be of small diameter, and the holes in the cork made with extra care. For preparing gases which are evolved without the necessity of applying heat, such as hydrogen and carbon dioxide, wide-mouthed bottles will answer quite as well as flasks.

37. **Thistle Funnels**. In place of these, ordinary funnels, attached to long pieces of glass tubing by india-rubber connectors, may be used. The connectors, however, will be slowly acted on if strong acids are brought in contact with them.

43. A simple form of **Spirit Lamp** is represented in fig. 105, next page. A cork is fitted to a wide-mouthed bottle, and a bit of glass tubing about 6 mm. in internal diameter and 8 cm. in length, passed through a hole bored in the cork, serves as the wick-holder. A small nick should be cut in the lower part of the side

of the cork to admit air, otherwise the spirit will not rise readily. A short wide test-tube is fitted over the cork as a cap, to prevent evaporation of the spirit when the lamp is not in use.



Fig. 105.

46. Flasks, and Retorts, the necks of which are broken, may be converted into evaporating dishes by leading a crack down from the broken part to within 5 or 6 cm. from the bottom, and then continuing it horizontally round the flask. A capsule about 5 cm. deep will thus be obtained, which will serve as well as, or even better than, a porcelain dish for evaporations, but cannot be used for ignitions. A clean iron spoon, not tinned, will often serve for the latter purpose.

48. A Drying Tube may be made out of a piece of glass tubing about 1.5 cm. in diameter and 15 or 20 cm. in length: a test-tube, if of stout glass, will answer the purpose, the closed end being drawn out to an external diameter of about 4 or 5 mm., so that an india-rubber connector will pass over it. The mouth of the tube may be then fitted with a cork and short piece of tubing as in fig. 23, p. 12. If a larger drying tube is required, a long, narrow paraffin-lamp-glass will answer well. If it is desired to use fragments of pumice soaked in hydrogen sulphate in order to dry a gas, the above form of drying tube cannot be used, as the acid which drains away would soon destroy the cork. A U-shaped tube must be obtained, or a tube such as is shown in fig. 106, may be made without much difficulty. A test-tube of thick glass is selected, about 2 x 20 cm. A portion of the glass about 3 cm. from the closed end is moderately heated all round, and then a pointed blowpipe-flame is directed upon one spot. The softened portion of the glass is forced inwards, by touching it with a piece of iron wire, so as to form a projection in the interior, reaching nearly to the centre. Two other similar projections are made by heating and pushing inwards other portions of the circumference, at the same distance from the closed end of the tube. Finally, the tube is annealed with especial care, the projections and the adjacent portions of the tube being heated again until the glass just begins to soften, and then cooled very slowly. A cork is now adapted to the tube, and fitted with two elbow tubes of small diameter, the one

having each of its branches about 6 or 8 cm. in length, the other having one branch about 6 cm. in length, and the other branch sufficiently long to reach, when the cork is fitted into its place, nearly to the bottom of the test-tube, passing between two of the projections.

In order to fill the tube, the cork should be loosened and raised just so far as to admit of its being turned half round and then rested on the rim of the tube. There will now be sufficient room left by the side of the cork to introduce, first four or five pieces of pumice rather larger than peas, which will rest upon the ledge formed by the projections, and then a quantity of smaller bits of pumice, until the tube is nearly full. Finally, a little concentrated hydrogen sulphate should be poured in through a funnel (care being taken not to wet the mouth of the tube), and the cork turned round again and gently pressed into its place. The acid will, as it descends, moisten the pumice, and any excess will collect at the bottom of the tube, and may be withdrawn by blowing through the short elbow tube, which will cause the acid to rise through the long tube.

One advantage of this form of drying tube is, that the pumice can be easily drenched with fresh acid, and the excess of acid withdrawn, without removing the pumice from the tube. Moreover, any number of these tubes can be arranged in an ordinary test-tube-stand, if required, or clustered together and held by india-rubber bands. A short wide-mouthed bottle forms a good support for a single tube, the latter being passed through a large hole in the cork.

70. Gas Blowpipes. The best form of portable blower is undoubtedly that lately brought out by Mr. Fletcher, of Warrington, which is represented in fig. 107, next page. In this, a piece of sheet india-rubber is stretched over a round disc containing a



Fig. 106

valve, screwed upon the top of the feeder; this sheet, when expanded to a hemisphere by blowing in air, forms the reservoir, and by its elasticity supplies the requisite pressure.

A similar blower may be made out of a common pair of bellows; the nozzle being stopped up, and two or three holes made in the centre of the upper board and covered with a flap of leather, nailed along one edge only, so as to act as a valve. Upon the upper board of the bellows should be fitted (by screws and glue) a thick wooden ring, having a groove cut in its rim as if for a pulley, but close to the upper edge. Just below this groove a hole should be bored in the direction of a radius of the ring, to form an outlet for the compressed air; a bit of brass tube should be fitted tightly into it, with which india-rubber tubing may be connected, as in the figure. A circular piece of vulcanised sheet india-rubber¹ about

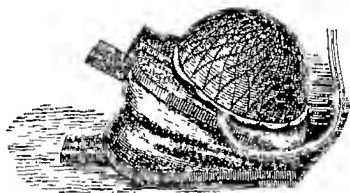



Fig. 107.

1 mm. thick should be laid on the wooden ring, and its edge secured air-tight in the groove by folds of wire or string. It will be advisable to place a net, or a calico bag, over the reservoir, and secure it also in the groove, so as to prevent the india-rubber expanding beyond a hemisphere and bursting. The bellows should be screwed to a base-board, one end being slightly tilted up by fixing a piece of wood under it, so as to allow air to enter the lower valve. A couple of  shaped springs of thick brass or iron wire should be fitted, one on each side of the bellows, in order to keep the upper board raised except when pressed upon by the foot.

¹ If there is any difficulty in procuring india-rubber sheet, a large bladder may be cut in half, and one hemisphere of it may be secured by its edge in the groove as above described. In order to obtain the pressure, a couple of large india-rubber rings may be stretched across it, at right angles to one another, between nails or books driven in on opposite sides of the wooden ring: these will keep it flat until air is blown into it.

The blowpipe, for use with this blower may be made out of a brass T-piece fitted with an internal glass jet, as described just below.

A very cheap and simple gas blowpipe is represented in fig. 108.

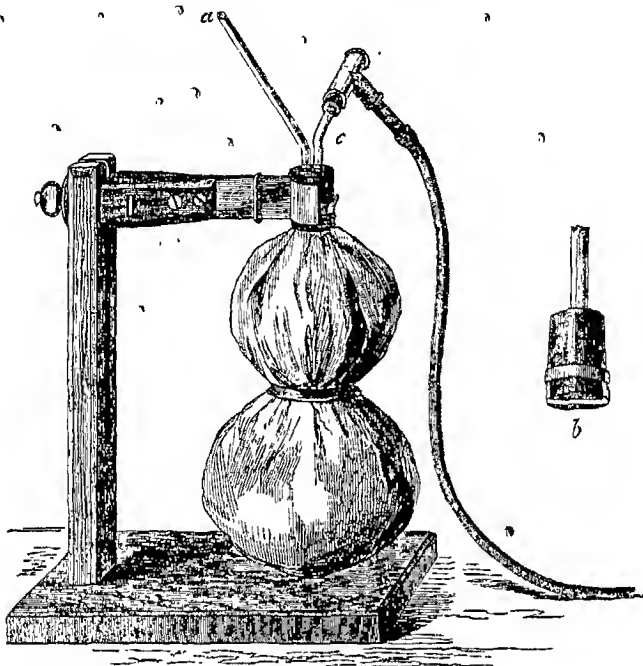


Fig. 108.

The air reservoir is a bladder, round which a large and strong india-rubber ring is placed to give it elasticity¹. The air is supplied at intervals from the lungs through the tube *a*, at the other end of

¹ A bladder, when allowed to dry, loses most of its pliability. To keep it moist and fit for use, it should be rubbed over with some glycerine, diluted with an equal bulk of water (a few drops of carbolic acid being added, to prevent putrefaction), a little of the liquid being also poured into the interior.

Another method of preserving a bladder is to allow it to dry in a distended state, and then to rub over it a rag dipped in sweet oil, a little oil being also poured inside. If the bladder is now twisted and worked in all directions between the hands, it will become permanently pliable, and will not have the unpleasant smell of a moist bladder.

which is a valve to prevent the return of the air. This valve is represented in full size at *b*, and is thus constructed. A cork about 1.5 cm. in diameter is selected and a hole bored through it, into which the tube *a* is fitted so that its extremity may be just level with the surface of the cork. Across the end of the cork is laid a strip of oiled silk (oilskin) about 1 cm. or rather less in breadth, and its ends are turned down on each side of the cork and secured by an india-rubber ring, or folds of thread. The mouth of the bladder is closed by a cork about 2 cm. in diameter through which two holes are pierced: into one the tube *a* is fitted; into the other a short tube *c*, bent to an obtuse angle, and terminating in a jet. Over this jet is fitted by a cork a common 'three-eighths T-piece' (which may be obtained from any gas-fitter); and to the side-branch of this latter is adapted a short piece of glass (or, better, brass) tubing, to be connected with the gas supply. The valve having been fitted to the tube *a*, the cork is placed in the neck of the bladder, and tightly secured by several folds of string; the whole may then be supported in a Bunsen's holder, and the gas turned on and lighted at the open end of the T-piece. On blowing into the tube *a* the bladder will become distended with air, which will be forced out through the jet by the elasticity of the india-rubber ring. A very good and fairly uniform brush-flame may be thus obtained, quite hot enough for most glass-blowing operations. Moreover, with a small air-jet, a low pressure of air, and a limited supply of gas, a well-defined pointed flame may be formed, which answers well for analytical blowpipe operations. The air-jet should not, in any case, be made larger than 1 mm. in diameter, otherwise the labour of supplying air from the lungs becomes considerable. An obvious expedient for avoiding this labour is, to connect the tube *a* by a long piece of india-rubber tubing with the nozzle of a common pair of bellows; the latter being fixed in a frame or box and placed on the floor. The upper board of the bellows may be kept raised by a spring (or by an india-rubber band, attached to the frame) and pressed down by the foot.

The gas should not be left burning at the end of the T-piece longer than is required, since the latter will get very hot, and the cork may be loosened. Indeed it is decidedly better to have a brass jet screwed in; but this will add to the expense. The materials for such a blowpipe as is above described will not cost more than 1s. 6d.

In order to get the full effect of the very high temperature of the

blowpipe-flame, it is necessary to surround it with a casing or furnace of fire-clay, to prevent loss of heat by radiation. A very convenient gas-furnace of this kind is shown in fig. 109, in which a temperature fully sufficient for all ordinary chemical operations, such as decomposition of silicates (p. 311), &c., and even for melting iron and steel can be readily obtained and kept up.

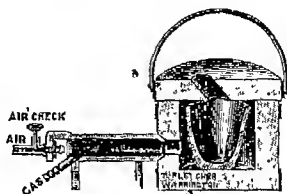


Fig. 109.

As a substitute, a few bricks, or lumps of pumice or coke can be easily arranged so as to form a cavity in which the crucible should be placed, and into which the flame of the blowpipe should be directed.

110. A Retort and Receiver for distillations on a small scale are represented in fig. 110.

The retort is a very small flask, or a test-tube having its lower end expanded into a bulb. This is connected by an india-rubber joint with a tube nearly as large as the neck of the flask or test-tube, which is drawn out to a diameter of 2 or 3 mm. and a length of 15 cm. or more, and then bent to an acute angle near the commencement of the drawn-out portion. The receiver is a test-tube, fitted with a cork through which the drawn-out portion of the connecting tube passes, reaching nearly to the closed end of the test-tube. The cork should have several

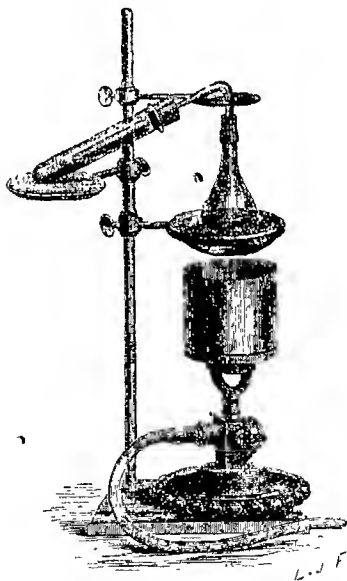


Fig. 110.

for uncondensable vapours, and the receiver may be placed in an evaporating dish filled with cold water, or snow. Nitrogen tetroxide

may be readily condensed in such an apparatus, but the tube should be fitted to the flask by a plug of asbestos mixed up with plaster of Paris, on account of the corrosiveness of the vapour.

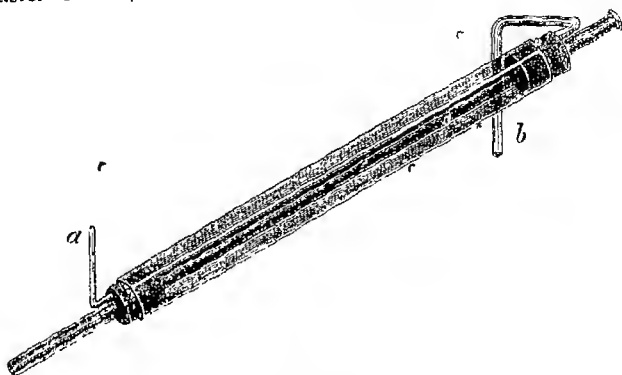


Fig. 111.

The best form of condenser is that known as 'Liebig's Condenser,' as shown in fig. 111.

It consists of a long straight tube surrounded by a wider tube ; in the space between the two a stream of cold water is kept constantly flowing.

Such a condenser may be easily made out of a long cylindrical lamp-glass, having corks fitted tightly to its ends. In the middle of each cork a hole should be bored, into which should be fitted a piece of glass tubing about 1 cm. in diameter, or rather less. One end of this should project 3 or 4 cm. beyond the cork, and the beak of the retort should be connected with it by a ferule of india-rubber tubing secured with string¹. The other end of the tube may project 10 or 12 cm. beyond the cork, and enter the receiver.

Into the corks should also be fitted small tubes bent as shewn in the engraving. The end of the lower one, *a*, should be connected by an india-rubber tube, with pinch-cock, to a large jug or bottle of cold water, placed on a higher level (the bottle with siphon arrangement shewn in fig. 115, p. 549, will do very well).

¹ If strong acids are to be distilled, it is better to make the beak of the retort enter the condensing tube a little way; the end of the latter being bordered and expanded by the method explained on p. 44. The beak of the retort may be drawn out slightly until, when a ferule of india-rubber tubing is fitted over it, it will just fit tightly into its place.

Under the end of the other tube, *b*, a jug should be placed, to catch the waste warm water, or the water may be led off at once into the sink.

A Screw Pinch-cock, which serves to check or stop the flow of a gas or liquid through india-rubber tubes, may be made by cutting out two strips of stout tin plate about 6×1.5 cm., turning over a narrow portion on each side, to give additional stiffness, boring a hole at each end (which may be done with a bradawl driven through by a hammer), and connecting the two strips by a couple of the small nuts and screws used for holding papers or letters together, which may be procured from a stationer's. Fig. 112 shows a pinch-cock thus made. Strips of hard wood, such as beech or box, may be used instead of the strips of tin.



Fig. 112.

Gas Apparatus. For preparing small quantities of such gases as oxygen or ethylene, a large test-tube may be used, fitted with a cork and delivery-tube as shown in fig. 113. Gases requiring no heat in their preparation, such as hydrogen, may be made in ordinary wide-mouthed bottles, fitted with cork, thistle-funnel, and delivery tube. A convenient apparatus for obtaining a constant stream of a gas, such as hydrogen sulphide,

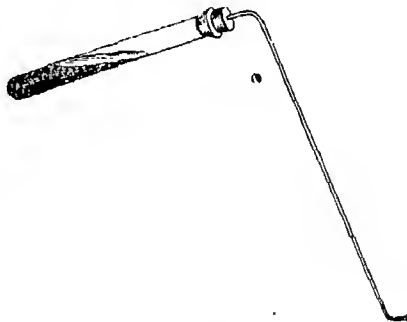


Fig. 113.

which may be generated without the application of heat, is represented in fig. 114, next page. A paraffin-lamp-glass (one of those which bulge out near the middle) is obtained, and a cork is fitted to its lower extremity. In this cork five or six holes are bored, and before being finally fitted into its place it is thoroughly saturated with wax or paraffin, to protect it from the action of acids¹. Some

¹ This may be done by placing it for several minutes in a dish containing some paraffin or wax heated a little above its melting-point over a lamp.

lumps of iron sulphide are placed in the glass, and a cork with a short elbow tube is fitted into the upper end of the glass, a piece

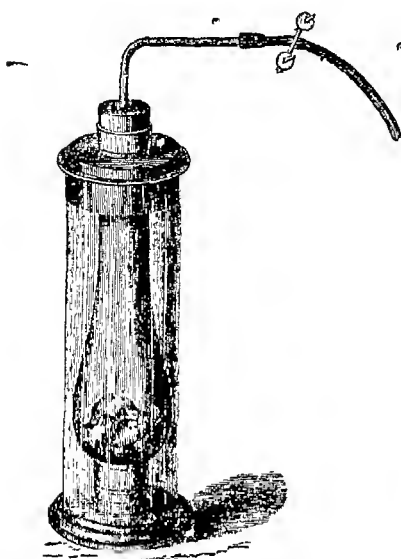


Fig. 114.

of india-rubber tubing, carrying a screw pinch-cock, being adapted to the outer end of the elbow tube. The glass is now lowered into a tall wide-mouthed bottle or jar (the pinch-cock being closed), and the latter is filled nearly to the neck with common hydrogen chloride, previously diluted with twice its bulk of water, and allowed to cool. When the pinch-cock is opened, the acid will rise through the holes in the cork, and will act upon the iron sulphide, causing an evolution of hydrogen sulphide, which may be led into a flask or tube, as required. When the pinch-cock is closed, the gas

collects in the glass, and finally drives the acid back into the outer bottle; the evolution of gas ceasing when the acid is withdrawn from contact with the iron sulphide. The lamp-glass should be retained in its place in the bottle by being passed through a bung fitted into the neck of the latter, and having one or two nicks cut in it to admit air. The same form of apparatus will, of course, serve for other gases, such as hydrogen or carbon dioxide.

A simple form of gas-holder, which may be easily constructed and will be found very useful, is represented in fig. 115. The bottles used are those which are known by the name of 'Winchester quarts,' and which may be procured from any chemist. A cork is adapted to one of the bottles, A, and fitted with two elbow tubes, the one, *c*, having both its branches about 8 or 10 cm. long, the other, *d*, having one branch long enough to reach to the bottom of the bottle. An elbow tube, *e*, similar to this latter is

fitted to the other bottle, B, by a cork which has a nick cut along it, so as to admit air. The two tubes last mentioned, *d* and *e*, are connected by a piece of india-rubber tubing about 40 or 50 cm. in length, over which is slipped a screw pinch-cock. A piece of india-rubber tubing, also carrying a pinch-cock, is connected with the short elbow tube, *c*. All the connections must be made tight by folds of string or wire.

In order to use the apparatus, the bottle, A, is completely filled with water, the cork with the two elbow tubes being temporarily withdrawn. The india-rubber tube attached to the short elbow tube, *c*, is then connected with the delivery tube of the gas-generating flask, and gas is passed into the bottle, both pinch-cocks being opened.

The gas displaces the water in the bottle, which passes over into the other bottle, B; the latter being supported at such a height that there may never be more than a slight difference in level between the water in the two bottles, but that the gas may always pass in under slight pressure. When the first bottle is full of gas, both pinch-cocks should be closed, and the generating flask should be at once disconnected from the apparatus. If, now, a constant stream of gas is required, *e. g.* for burning at a jet, the bottle B (now full of water) should be placed on a stand or shelf, as shown in the figure, at such a height that its bottom may be a little above the level of the neck of the other bottle. If the pinch-cock on the tube connecting the two bottles is now opened, water will flow from the upper into the lower one, and will exert a pressure on the gas contained in the latter. It will then only be necessary to open the other pinch-cock cautiously, in order to obtain a regular stream of gas.

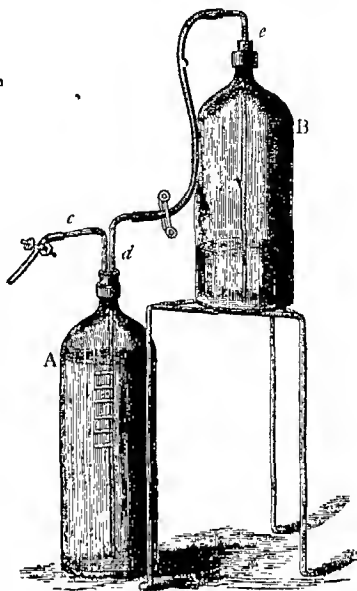


Fig. 115.

APPENDIX B.

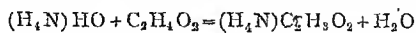
I.

PREPARATION OF NORMAL SOLUTIONS OF REAGENTS.

It is intended that these solutions shall be made of such a strength that volumes which bear a simple relation to each other may contain weights of the different substances which correspond to the weights indicated by their chemical formulae, *i. e.* to the weights of their molecules.

There is no extra trouble and there are very obvious advantages in adopting such a system in place of the usual one of dissolving 1 part of the substance in 10 or 15 parts of water without strict reference to its molecular weight. It is clear that on the latter will depend the amount of chemical work which a given weight of the substance can do; and it would be wrong, or at least wasteful, to take for a solution the same weight of a sodium salt as of the corresponding potassium salt, when much less of the former than of the latter is required to effect a given amount of chemical change.

By carrying out the above principle the reactions between measured volumes of solutions become almost as simple as those between measured volumes of gases. For example, suppose that a little ammonium acetate is required for an experiment, such as expt. 3, p. 348. The reaction which occurs between ammonium hydrate and hydrogen acetate is expressed by the following equation:—



From this we learn that one molecule of each substance is required for the combination; thus, 35 hydrogen-atom-weights of ammonium hydrate, and 60 hydrogen-atom-weights of hydrogen acetate, or, at any rate, weights bearing that proportion to each other, must be taken; for instance, 35 centigrammes of ammonium hydrate, and 60 centigrammes of hydrogen acetate. If, then,

the ordinary laboratory solutions of these substances are so made that 5 c.c. of them contain the above weights, the ammonium acetate can be made at once by simply mixing *equal volumes* of the solutions.

It has been found most convenient to take the centigramme as the practical unit of weight, corresponding to the hydrogen-atom-weight, which is, of course, a small but definite fraction of it; and the weights indicated by the formulae printed in italics are to be understood to mean centigrammes, instead of hydrogen-atom-weights, as usual. Thus $(H_4N)_2CO_3$ expresses a weight of 96 centigrammes of ammonium carbonate, and ' $(H_4N)_2CO_3$ in 5 c.c.' means that 5 c.c. of the solution contain 96 centigrammes of the salt.

[Reagents, even though procured, as they ought to be, from a trustworthy chemist, are liable to contain impurities; and before use they should be invariably tested with care, and rejected at once (at least for analytical purposes) if found impure¹.

The more usual impurities are mentioned in connection with each substance, together with simple tests for detecting them.

In the following directions, although 100 c.c. is mentioned in all cases, yet it will be well to prepare five or ten times this quantity of some solutions, such as dilute hydrogen sulphate, which are constantly required.]

1. Ammonium Carbonate ($(H_4N)_2CO_3$ in 5 c.c.). Dissolve 17 grms. of the pure white sublimed salt in 75 c.c. of distilled water, add 15 c.c. of solution of ammonium hydrate (sp. gr. 0.96)², place the solution in a measure, and add more water until the whole measures 100 c.c.

The salt often contains ammonium chloride and sulphate, and also iron chloride. If either of the two latter are present the salt is unfit for use, and another sample should be obtained.

(a) Heat a small piece of it on perfectly clean platinum foil over a Bunsen's burner. It should volatilise entirely.

(b) Add to a portion of the solution in a test-tube a drop of ammonium sulphide. If the solution becomes dark, or if a black precipitate is formed, iron is probably present.

(c) Add to another portion of the solution pure dilute hydrogen

¹ In most cases, where the quantity purchased is small, it will probably be best to exchange it for a pure sample, and not to attempt to purify it yourself.

² Instead of this, 5 c.c. of the strongest solution ('Liq. Ammon. fortiss.', sp. gr. 0.88), may be used, if at hand.

nitrate, drop by drop, until no further effervescence occurs and a drop of the liquid placed on blue litmus-paper turns it decidedly red: then add a drop of solution of barium chloride. If a cloudiness is produced, a sulphate is probably present.

(d) Acidify another portion with hydrogen nitrate, as in c, and add a drop of solution of silver nitrate. If a cloudiness is produced, a chloride is probably present.

2. **Ammonium Chloride** ($(H_4N) Cl$ in 5 c.c.). Dissolve 10.7 grms. of the pure salt in 80 c.c. of water, and dilute with water to 100 c.c.

The salt may contain ammonium sulphate and iron chloride. It should be tested in the same manner as the carbonate (with the omission of expt. d), and rejected, except for making ammonia, if found impure. Both these impurities may be removed by recrystallisation.

3. **Ammonium Hydrate** ($(H_4N) HO$ in 5 c.c.). Dilute 50 c.c. of solution of ammonia (sp. gr. 0.96, containing 7 grms. of ammonium hydrate in 100 c.c.) with water to 100 c.c.

If the concentrated solution (sp. gr. 0.88) is at hand, 20 c.c. of it may be diluted with water to 100 c.c.¹

The solution should leave no residue on evaporation at a temperature not much above 100°, and should give little or no precipitate on addition of an equal volume of lime water.

4. **Ammonium Molybdate** ($(H_4N) HMoO_4$ in 30 c.c.). Dissolve 6 grms. of the salt in 20 c.c. of solution of ammonium hydrate (sp. gr. 0.96) by a gentle heat; pour the solution slowly, with constant stirring, into 60 c.c. of dilute hydrogen nitrate (equal volumes of the strong acid and water): dilute it to 100 c.c. and allow it to stand for at least a day before filtering it, in order that any traces of ammonium phospho-molybdate may separate.

The solution should contain so large an excess of acid that little or no precipitate (of molybdic acid) forms when it is heated to boiling.

5. **Ammonium Oxalate** ($(H_4N)_2 C_2O_4$ in 5 c.c.). Dissolve 2.84 grms. of the salt in 60 c.c. of water, and dilute to 100 c.c.

¹ Since the strength of solution of ammonia is liable to vary, owing to the volatility of the substance, it will be best to see whether the solution is of approximately the right strength by putting 10 c.c. of it into a test-tube, adding a drop or two of solution of litmus, and seeing whether 5 c.c. of dilute hydrogen sulphate (20) are sufficient to neutralise it. It should be made rather too strong than too weak, since it loses strength on keeping.

6. Ammonium Sulphide ($(H_4N)_2S$ in 5 c.c.). The solution usually sold varies in strength, but may generally be diluted with three times its bulk of water for use.

It may be easily prepared by saturating 50 c.c. of solution of ammonium hydrate (sp. gr. 0.96) with hydrogen sulphide (p. 275), and then adding 50 c.c. of the same solution of ammonium hydrate.

The solution is colourless at first, but soon becomes yellow, owing to the formation of ammonium polysulphides. It still, however, remains fit for use in analysis for some time; but when it begins to deposit sulphur, turning colourless again, it should be thrown away.

The solution is liable to contain a sulphate, and possibly a calcium salt. Test one portion for a sulphate with a drop of solution of barium chloride, and another portion for a calcium salt with solution of ammonium oxalate. No precipitate should be produced in either case.

7. Barium Chloride ($BaCl_2$ in 50 c.c.). Dissolve 5 grms. of the crystallised salt ($BaCl_2, H_2O$) in 80 c.c. of water, and dilute to 100 c.c.

The purity of the salt may be tested as follows. Place about 5 c.c. of the solution in a test-tube, heat it nearly to boiling, and add a slight excess of dilute hydrogen sulphate. While the precipitate of barium sulphate is subsiding, get ready a filter (of Swedish paper), wash it two or three times with warm water, then filter off the barium sulphate and evaporate the filtrate to dryness on a clean watch-glass. No solid residue should be left.

The test will not, however, serve to show whether lead is present, as it frequently is. Its presence may be suspected if the solution becomes dark in colour when mixed with some solution of hydrogen sulphide.

8. Calcium Chloride ($CaCl_2$ in 10 c.c.). Dissolve 11.1 grms. of the dry salt (or 22 grms. of the crystallised salt) in 80 c.c. of water, and dilute to 100 c.c.

The salt often contains iron perchloride, from which it may be purified by crystallisation from a small quantity of water. The solution should be quite neutral to test-paper, and should not become dark coloured, or give a precipitate, when a drop of solution of ammonium sulphide is added.

9. Calcium Hydrate (CaH_2O_2 in 540 c.c.). For the method of making this solution, see p. 66.

10. Calcium Sulphate ($CaSO_4$ in 500 c.c.). This solution

should be made in the same manner as that of calcium hydrate, about 5 grins. of the best plaster of Paris being shaken up with 200 c.c. of water, and allowed to stand for a day or two, with occasional shaking, before being filtered.

11. **Chlorine, solution of.** For preparing this, an apparatus similar to that used for preparing solution of hydrogen sulphide (p. 275) should be set up. The small wash-bottle is necessary in this case, to retain hydrogen chloride which may distil over: the other bottles need not be so large as those used for hydrogen sulphide, as less of the solution of chlorine is likely to be wanted, and it does not keep well.

Prepare the gas as already directed (p. 230), and pass it into the water until the latter assumes a perceptible yellow colour. It will be better to stop short of the point of saturation, as a comparatively weak solution of chlorine is all that is required for analytical purposes. It should be kept in a stoppered bottle, protected carefully from the light, which causes its decomposition¹. A good method of protecting it is, to paste over the bottle two or three thicknesses of brown paper, through which, when it is dry, two narrow slits should be cut on opposite sides of the bottle, in order that the quantity of solution contained in the bottle may be seen.

12. **Cobalt Nitrate** ($Co(NO_3)_2$ in 20 c.c.). Dissolve 7.25 grms. of the crystallised salt in 40 c.c. of water, and dilute to 50 c.c.

13. **Copper Sulphate** ($CuSO_4$ in 25 c.c.). Dissolve 10.7 grms. of the crystallised salt [$CuSO_4 \cdot (H_2O)_5$] in 80 c.c. of water, and dilute to 100 c.c.

14. **Hydrogen Acetate** ($HC_2H_3O_2$ in 5 c.c.). Place 70 c.c. of the acid sold as 'Acid. Acet. Fort.' (sp. gr. = 1.04; containing 33 per cent. of hydrogen acetate) in a measure, and dilute with water to 100 c.c. [The best and purest acid is the 'Glacial Acetic Acid' (sp. gr. = 1.065; containing 84 per cent. of hydrogen acetate), which is solid at 10° C. (50° F.): if this is at hand, 18 c.c. of it may be put into a measure and diluted with water to 100 c.c.] It will be well to try whether 5 c.c. of this approximately neutralises 5 c.c. of solution of ammonium hydrate (No. 8). It often contains a chloride and a sulphate, but traces of these will not interfere with its use in analysis.

¹ The bottles of deep yellow glass, used in photography, answer very well for this purpose.

(a) Evaporate a portion of the acid on a watch-glass. It should leave no residue.

(b) To another portion add three or four drops of dilute hydrogen nitrate, and then a drop of solution of silver nitrate. If a cloudiness is produced, a chloride is present.

(c) To another portion add a drop of solution of barium chloride. If a cloudiness is produced, a sulphate is present.

15. **Hydrogen Chloride** (HCl in 1 c.c.). The acid of which the sp. gr. is 1.158 is very nearly of the right strength. It is liable to contain a sulphate, and also iron and arsenic, and must, for analytical purposes, be obtained free from these impurities.

(a) Dilute a portion with three or four times its volume of water, and test for a sulphate by solution of barium chloride.

(b) The presence of iron is generally indicated by the yellow colour of the acid. Add to a portion a drop of hydrogen nitrate, and boil the mixture for a few seconds; then add an equal volume of water, and allow it to cool. If the liquid turns red on addition of a drop of potassium thiocyanate, iron is present.

(c) Arsenic must be tested for by Reinsch's method (p. 371), or by Marsh's method, which may be tried in a test-tube (expt. 5 (a), p. 369).

16. **Hydrogen Chloride**, dilute (HCl in 5 c.c.). Place 20 c.c. of the strong acid in a measure, and dilute with water to 100 c.c.

17. **Hydrogen Nitrate** (HNO_3 in 1 c.c.). The acid of which the sp. gr. is 1.3 is very nearly of the right strength. It is liable to contain lower nitrogen oxides, and also a sulphate and a chloride.

(a) It should leave no residue when evaporated on a watch-glass.

(b) It should be nearly or quite colourless. If it is yellow, lower nitrogen oxides are present. These, however, are usually found in the acid when it has been exposed to light, and do not in general interfere with its use in analysis.

(c) When separate portions are diluted with water and tested with solution of barium chloride and silver nitrate, no cloudiness should be produced in either case.

18. **Hydrogen Nitrate**, dilute (HNO_3 in 5 c.c.). Place 20 c.c. of the strong acid in a measure, and dilute it with water to 100 c.c.

19. **Hydrogen Sulphate** (H_2SO_4 in 0.55 c.c.). The acid of which the sp. gr. is 1.845 is very nearly of the right strength. It may contain lead and arsenic, and also a nitrate, and must, for analysis, be obtained free from these impurities.

(a) Evaporate a few drops on a porcelain dish, taking care not to inhale the dense white fumes of the acid. No solid residue should be left.

(b) Dilute a few drops of the acid with 2 or 3 c.c. of water. If the mixture becomes turbid, lead is present.

(c) Dilute 2 or 3 c.c. of the acid with an equal volume of water : add *one* drop (not more) of indigo sulphate, and boil the mixture. If the blue colour of the indigo disappears, a nitrate is present.

(d) Arsenic should be tested for as directed in reference to hydrogen chloride (15, p. 555).

20. Hydrogen Sulphate, dilute (H_2SO_4 in 5 c.c.). Measure out 60 c.c. of water into a beaker and add by degrees 11 c.c. of the strong acid, stirring the mixture continually with a glass rod. When the liquid is cool, pour it into the measure, and dilute to 100 c.c.

21. Hydrogen Sulphide, solution of. Directions for making this are given on p. 275. The bottle containing the solution should be always kept well corked and inverted, with its neck immersed in water.

22. Iron Perchloride (Fe_2Cl_6 in 50 c.c.). Dissolve 2.25 grms. of fine iron-wire in about 30 c.c. of dilute hydrogen chloride, heating the mixture in a small flask and adding a little strong hydrogen chloride when the action becomes slow. When all the iron is dissolved, pour the solution into a porcelain dish, and add strong hydrogen nitrate, a few drops at a time, as long as the addition of a drop produces a transient brown colour in the liquid. The excess of acid may then be driven off by evaporating it, on a water bath, to a small bulk (not to complete dryness). Finally, dilute it with water to 100 c.c. and filter it.

23. Iron Protosulphate ($FeSO_4$ in 50 c.c.). Dissolve 5.5 grms. of the pure green crystals [$FeSO_4$, (H_2O)₇] in 60 c.c. of cold water, with addition of about 5 c.c. of dilute hydrogen sulphate, and dilute with water to 100 c.c. Owing to the great tendency of iron protosalts to absorb oxygen and pass into persalts, the solution cannot be preserved unaltered for any length of time, and will contain an increasing quantity of iron persulphate the longer it is kept. This tendency is lessened by the addition of acid as above recommended, and also by keeping a little iron-wire in the bottle.

Instead of the above, it is a decided advantage to use iron-ammonium sulphate [$Fe(H_4N)_2(SO_4)_2$, (H_2O)₆] (a salt now

easily and cheaply procurable), which shows much less tendency to become oxidised. The solution may be made as above directed, 8 grms. of the salt being taken.

24. **Lead Acetate** ($Pb(C_2H_3O_2)_2$ in 50 c.c.). Dissolve 6.5 grms. of the salt in 80 c.c. of water, with the addition of one or two drops of hydrogen acetate, and dilute to 100 c.c.

25. **Litmus, solution of.** This may be bought ready made; but it is best to buy a little of the solid, and boil 2 or 3 grms. of it (previously powdered) with 110 c.c. of water, and filter the deep blue solution obtained. This may be kept for a long time unaltered, if two or three drops of carbon disulphide are added, and a little powdered chalk.

26. **Magnesium Sulphate** ($MgSO_4$ in 50 c.c.). Dissolve 5 grms. of the salt in 90 c.c. of water, and dilute to 100 c.c.

27. **Mercury Perchloride** ($HgCl_2$ in 100 c.c.). Dissolve 3.2 grms. of the crystallised salt in 80 c.c. of water, and dilute to 100 c.c.

28. **Platinum Perchloride** ($PtCl_4$ in 50 c.c.). A comparatively small quantity of this substance will be required, and it will on the whole be best to purchase it in the state of solution (3.2 grms. of the salt dissolved in 50 c.c. of water). The method of obtaining it from platinum scraps and residues (which, however, often contain iridium, see note, p. 393) is given in the next section of this Appendix.

29. **Potassium Chromate** (K_2CrO_4 in 50 c.c.). Dissolve 4 grms. of the salt in 80 c.c. of water, and dilute to 100 c.c.

The salt often contains a sulphate, from which it is difficult to free it by recrystallisation. This should be tested for by barium chloride, after strongly acidifying the solution with hydrogen nitrate (to prevent the precipitation of yellow barium chromate). If a sulphate is found, it will be best to prepare the test-solution by taking (instead of the chromate) 8 grms. of potassium dichromate, a salt which is usually met with in a much purer condition.

30. **Potassium Ferricyanide** ($K_3Fe(CN)_6$ in 50 c.c.). Dissolve 6.6 grms. of the salt in 80 c.c. of water, and dilute to 100 c.c. The solution, especially if it has been kept for a month or two, is liable to contain traces of potassium ferrocyanide. It should give no blue precipitate, but only a brown colouration, when tested with a drop of a solution of pure iron perchloride.

31. **Potassium Ferrocyanide** ($K_4Fe(CN)_6$ in 50 c.c.). Dissolve 8.4 grms. of the salt in 80 c.c. of water, and dilute to 100 c.c.

Potassium ferricyanide is sometimes present as an impurity; it may be detected by adding to a portion of the solution a drop of solution of silver nitrate. If a reddish-brown and not a white precipitate is found, potassium ferricyanide is present. The salt may easily be purified by recrystallisation.

32. Potassium Hydrate, (KHO in 5 c.c.). Dissolve 11 grms. of the substance (which is sold in sticks) in 80 c.c. of water, laying a watch-glass on the mouth of the flask, to prevent absorption of carbon dioxide from the air. When the solution is cool, pour it into the measure, and dilute to 100 c.c.; then transfer it without loss of time to a stoppered bottle, which should not be made of flint glass. The solution attacks the glass of the bottles in which it is kept, and soon takes up carbon dioxide from the air. A fresh solution should therefore be made from time to time; and for some experiments it will be best to dissolve a small lump of the substance in water and use it at once.

If any deposit forms in the bottle, it should be separated by decantation, not filtration.

The best potassium hydrate is that which has been purified by solution in alcohol (in which most of the impurities, *e.g.* carbonate, are insoluble), the solvent being afterwards driven off by heat; but this is too expensive to be used in ordinary work.

The usual impurities are—a carbonate, an aluminate, a silicate, a chloride, and a sulphate, of which the last two are not important. Traces, at any rate, of the three first-mentioned impurities will be found in a solution which has been kept some time: the carbonate derived from the carbon dioxide in the air, the aluminate and silicate from the glass of the bottles.

(a) Add to a portion of the solution pure dilute hydrogen nitrate, until a drop of the liquid placed on blue litmus-paper colours it decidedly red. No effervescence (or only a slight one) indicative of the presence of a carbonate should be produced.

(b) Test one portion of the solution which you have acidified with hydrogen nitrate, for a sulphate, by adding a drop of solution of barium chloride.

(c) Test another portion of the same solution for a chloride, by adding a drop of solution of silver nitrate.

(d) Mix some of the solution of potassium hydrate with an equal volume of solution of ammonium chloride, and boil the solution. If a flocculent, semi-transparent precipitate is formed after a little time, an aluminate or silicate is present.

33. Potassium Iodide (KI in 50 c.c.). Dissolve 3.3 grms. of the salt in 80 c.c. of water, and dilute to 100 c.c.

The salt often contains a little potassium iodate. It should be bought in the form of colourless, well-defined cubic crystals. The solution should not turn yellow at once when one or two drops of pure dilute hydrogen sulphate are added.

34. Potassium Thiocyanate ($KCNS$ in 50 c.c.). Dissolve 2 grms. of the salt in 80 c.c. of water, and dilute to 100 c.c.

35. Silver Nitrate ($AgNO_3$ in 50 c.c.). Dissolve 3.4 grms. of the salt in 80 c.c. of water, and dilute to 100 c.c.

36. Sodium Carbonate (Na_2CO_3 in 10 c.c.). Dissolve 28.6 grms. of the pure crystallised salt [$Na_2CO_3 \cdot (H_2O)_{10}$] in 80 c.c. of water, and dilute to 100 c.c. [Instead of this, 10 grms. of the anhydrous salt may be taken.]

The salt is liable to contain sodium sulphate and chloride, and should, for analytical purposes, be free from these impurities.

Add to a portion of the solution dilute hydrogen nitrate as long as an effervescence occurs, warm the liquid until the carbon dioxide is completely expelled, and divide it into two portions. Test one portion for a sulphate by adding a drop of solution of barium chloride, and the other portion for a chloride by adding a drop of solution of silver nitrate. No precipitate should be produced in either case.

37. Sodium-Hydrogen Phosphate (Na_2HPO_4 in 50 c.c.). Dissolve 7.2 grms. of the salt in 50 c.c. of water, and dilute to 100 c.c.

The salt is liable to contain a chloride and a carbonate. These impurities should be tested for in the manner described under the head of Potassium Hydrate, p. 558.

38. Sodium-Hydrogen Tartrate ($NaHC_4H_4O_6$ in 50 c.c.). Dissolve 3.8 grms. of the salt in 80 c.c., and dilute to 100 c.c.

The solution does not keep for any great length of time, a growth of fungus soon appearing in it. When a little of it does not give an almost immediate crystalline precipitate on addition of one drop of solution of potassium hydrate (see p. 217), it should be thrown away.

39. Starch, solution of. Heat 100 c.c. of water to boiling in a flask or beaker. Weigh out 1 gm. of pure white starch, and mix it thoroughly with 4 or 5 c.c. of cold water in a test-tube. When the water in the flask boils, take away the lamp, and, as soon as the boiling has ceased, pour the starch *little by little* into the water,

shaking after each addition. The starch granules swell and burst, their transparent contents being scattered through the liquid, giving the appearance of having dissolved in it. Replace the lamp, and boil the liquid again for a minute, stirring or shaking it all the time: then allow it to cool slightly and filter it¹, but do not use it for testing until it is quite cool.

The solution does not keep well, the starch being gradually converted into dextrine, which gives a brownish violet colour with free iodine, instead of the characteristic deep blue formed by starch.

The addition, however, of about one-twentieth of its volume of hydrogen acetate seems to preserve it in good condition for at least six months.

40. Tin Protochloride ($SnCl_2$ in 50 c.c.). Boil 3 gms. of pure tin foil with 10 c.c. of strong hydrogen chloride until the metal is nearly all dissolved; then dilute the solution with water to 50 c.c. and filter it into a bottle in which some pieces of granulated tin have been placed.

An excess of the metal should always be kept in the bottle to prevent the formation of any perchloride, and if the solution becomes turbid, 2 or 3 c.c. of strong hydrogen chloride should be added.

II.

RECOVERY OF SILVER, GOLD, AND PLATINUM FROM RESIDUES.

1. Treatment of Silver Residues.

It has been already recommended (p. 318) that all waste solutions containing silver should be poured into a stock-bottle kept for the purpose, in order that when a sufficient quantity has accumulated the metal may be recovered from the mixture. The first step will be the conversion of any soluble silver salts which may

¹ This, although a rather tedious operation (since the pores of the filter soon get clogged) and not necessary for general work, results in a decided gain in the sensitiveness of the test.

be present into soluble silver chloride, by the addition of a considerable excess of common hydrogen chloride. This, if added in sufficient quantity, will even throw down any silver chloride which may have dissolved in sodium thiosulphate. It is convenient to keep some of the acid always in the stock-bottle, so as to decompose the silver salts as soon as they are put in. The mixture, after being warmed in a flask and shaken, should be filtered, and the precipitate thoroughly washed, first with dilute hydrogen chloride and then with water; and finally dried by placing the filter containing it in a porcelain dish on the sand-bath. When it is thoroughly dry, it must be shaken out of the filter, and mixed in a mortar with twice its weight of dried sodium carbonate and one-tenth its weight of potassium nitrate, some borax being also added to act as a flux. While the mixture is being made, a common Cornish clay crucible, about 12 or 13 cm. in height, should be gradually heated by being placed mouth downwards on the top of an ordinary fire, if there is no wind-furnace at hand. When it is thoroughly warmed, it may be turned up and surrounded with hot coals. When it becomes red-hot, the mixture should be thrown into it, little by little, with an iron spoon, the fire being urged by a pair of bellows, so as to keep the crucible at a full red heat. The mixture will at first effervesce considerably, and should be stirred with an iron rod to prevent its frothing over, but it will finally, when a bright yellow heat is attained, fuse into a clear fluid, under which the silver will collect in a button. When this takes place, the crucible must be kept at the highest possible temperature for about five minutes longer, the contents being occasionally stirred to hasten the aggregation of the small particles of reduced silver disseminated through the mass. Finally, the crucible should be lifted from the fire by a pair of tongs, and the fluid mass poured out on an iron plate, such as a sand-bath, placed on some sand. When cold the silver may be separated from the flux by breaking off the latter with a hammer; and boiling the ingot with water to separate the last traces of slag.

It is a good plan to re-melt the ingot of silver in a small clean crucible, sprinkling a little borax over it. When thoroughly melted the metal should be poured out as before on a piece of iron, and an approximate estimate of its purity may be formed by observing the degree of 'spirting' which takes place as the silver solidifies, owing to the escape of absorbed oxygen. Unless the metal be very pure and especially free from copper and lead, this spirting

will hardly take place at all, and the surface of the ingot will remain unruffled.

The lump of silver thus obtained may be either exchanged at a shop for the crystallised nitrate of silver, or it may be boiled for some time in a flask with hydrogen nitrate diluted with twice its volume of water, more of the acid being added when the action becomes slow¹. The solution should be evaporated to complete dryness, in order to drive off the excess of acid, the residue should be redissolved in water, and the solution, after filtration, should be evaporated down and left to crystallise, the basin being covered with a glass plate or a sheet of paper to exclude dust. The crystals should be drained in a funnel and dried on filter-paper. The mother liquor, on further evaporation, will yield another crop of crystals, and the liquid drained from these may either be poured into the 'silver residues' bottle, or reserved for purposes in which absolute purity is not required.

This is decidedly the best method of reducing silver residues, since not only the chloride, but also the sulphide, iodide, &c., are reduced by fusion with sodium carbonate. If, however, the chloride only has to be dealt with, it may be reduced by nascent hydrogen in the manner described on p. 320; the only disadvantages being that it is rather difficult to wash out the last traces of zinc salt from the spongy mass of silver, and also that organic impurities are liable to be carried down with the chloride, which form nitro-compounds when the metal is dissolved in hydrogen nitrate, and render the salt unfit for such delicate processes as photography.

2. Treatment of Platinum Residues.

These residues will usually contain the metal either as perchloride or as ammonium- or potassium-chloroplatinate. In the first place, add about one-tenth of the volume of strong solution of ammonium chloride (to separate any platinum which may be present in the solution), and evaporate the whole to dryness. Heat the residue to redness in a porcelain dish or a clean clay crucible, to get rid of any organic impurities, and to decompose the chloroplatinates. The resulting porous mass, to which any waste scraps of platinum foil

¹ If a perfectly pure salt is wanted, it will be necessary to precipitate the silver again as chloride from the solution in hydrogen nitrate, and to reduce it with pure sodium carbonate in the manner above described.

or wire may be added, should be thoroughly washed with warm water to remove all soluble salts, and then boiled for some time with a mixture of three parts of strong hydrogen chloride and one part of hydrogen nitrate, in a long-necked flask, having a test-tube full of cold water placed in the neck, to prevent loss of acid by evaporation. This will be best done in the open air, or at any rate the chlorous vapours must be led into a chimney or through a window, and not allowed to escape into the laboratory.

When the mixture has boiled for half an hour, the solution should be poured off, fresh acids added, and the boiling repeated. The solutions should then be mixed, and the whole evaporated at a gentle heat nearly, but not quite, to dryness, a little hydrogen chloride being added at the last, to decompose any remaining hydrogen nitrate. The solution of crude platinum perchloride, obtained by warming the residue with water, should be filtered and mixed with a saturated solution of ammonium chloride, which should be added until no further precipitate is thrown down. This precipitate, of ammonium chloroplatinate, should then be collected in a filter, and carefully washed with water to which about half its volume of common methylated spirit should be added, in order to prevent the loss of any considerable quantity of the salt, since ammonium chloroplatinate is not wholly insoluble in water. Lastly, it should be dried on the filter, and strongly heated in a porcelain dish, until the whole of the salt is decomposed (p. 394). The spongy platinum thus obtained should be dissolved in aqua regia, and evaporated down, at first over the lamp to a small bulk, and then on a water-bath¹ to complete dryness. The highly deliquescent residue should be transferred quickly to a well-stoppered bottle, or, better, dissolved at once in water for use.

A solution of convenient strength is made by weighing the spongy platinum before dissolving it in the acids, multiplying the weight in grammes by 25, and making up the solution to this number of cubic centimetres. This will give a solution 50 c.c. of which contains 3.39 grms. of platinum perchloride ($PtCl_4$ in 50 c.c.).

¹ In default of a regular water-bath for the above evaporations, the porcelain dish may be placed on the mouth of a beaker or saucepan rather smaller in diameter; the latter being previously half filled with water, which is kept gently boiling on a sand-bath.

3. Treatment of Gold Residues.

These may be worked up in the same way as platinum residues, except that the solution in aqua regia must, after evaporation, be mixed with excess of a strong solution of hydrogen oxalate, and boiled for some time. The gold will thus be precipitated in the metallic state, and the yellow spongy mass obtained will readily dissolve in aqua regia. The solution should be carefully evaporated on the water-bath, and the residue dissolved in water. For each gramme of gold taken, 50 c.c. of solution should be made. The liquid will then contain 3.03 grms. of gold perchloride in 100 c.c. ($AuCl_3$ in 100 c.c.).

APPENDIX C.

SHORT COURSES OF ANALYSIS FOR BEGINNERS.

[The use of these is referred to on p. 220. The general rules to be observed in making and writing out analyses, given on pp. 481-483, should be read over.]

I.

ANALYSIS

of a solution containing a salt which may contain any one of the following radicles : NITRATE, CARBONATE, ACETATE, TARTRATE, OXALATE. (The other radicle being potassium, sodium, ammonium, or hydrogen.)

[This solution will be always referred to as 'the original solution.']

[Test the action of the solution on litmus-paper. Take out a drop on a clean glass rod, and put it on a strip of blue litmus-paper. If it does not change the colour of the litmus, put another drop on reddened litmus-paper.

A The liquid does not decidedly alter the colour of either paper.

It is a solution of a neutral salt. Pass on to 2 (next page).

B The liquid reddens blue litmus-paper strongly (if only slightly, it may be considered as practically neutral).

Then it is probably a hydrogen salt, *i.e.* an acid. Pass on to 2 (next page).

C The liquid turns reddened litmus-paper strongly blue (if only slightly, it may be considered as practically neutral).

Then, out of all the radicles above mentioned, a CARBONATE is probably present.

To confirm this inference, pour about 5 c.c. of the original solution into a test-tube, and add several drops of dilute hydrogen sulphate. If a CARBONATE is present there will be an effervescence, owing to liberation of carbon dioxide.

To make sure that the gas is really carbon dioxide, dip the lower end of a pipette into lime water (calcium hydrate), withdraw it with a single drop of the solution remaining in the contracted portion, and lower it into the test-tube containing the gas, but not so far as to reach the solution; then suck a very little of the gas through the tube. If the lime-water becomes cloudy (seen by holding it up to the light) the gas is certainly carbon dioxide, and the solution certainly contains a CARBONATE.

- 2 Test for a . Put 4 or 5 c.c. of water into a test-tube, add about nitrate. half as much strong pure hydrogen sulphate, and one drop of indigo sulphate, and heat the mixture to boiling (the blue colour of the liquid should remain unaltered, see note¹). Add to this a few drops of the original solution and boil again. Observe if there is any change of colour.

A The blue colour of the indigo remains unaltered. If so, no nitrate is present. Pass on to 3.

B The blue colour of the indigo disappears.

Then the salt is a NITRATE.

To confirm this inference, put about 2 or 3 c.c. of the original solution into a test-tube, add an equal volume of strong hydrogen sulphate, and cool the mixture by holding it in a stream of water. When cold, hold the tube slanting, and pour gently down the side (from a pipette) some solution of iron protosulphate, so that it may float upon the liquid in the tube: then let the tube remain in the stand undisturbed, for 2 or 3 minutes. If a brown layer is formed where the two liquids meet, the solution certainly contains a NITRATE.

- 3 Test for a . Put about 6 or 8 drops of the original solution into tartrate. a test-tube, add about 5 c.c. of water, and enough solution of sodium carbonate to make the liquid alkaline to test-paper; then add 2 or 3 drops of solution of silver nitrate (which will produce a white precipitate), and boil the mixture, adding more silver nitrate if the precipitate re-dissolves. Observe whether the precipitate changes colour.

A It is unaltered or only turns light brown. If so, no tartrate is present. Pass on to 4.

It turns deep black.

¹ If the blue colour disappears, the hydrogen sulphate probably contains a trace of nitrate. In such a case, add another drop or more of indigo sulphate, until the liquid remains blue even on being boiled.

Then the solution contains a TARTRATE.

To confirm this, pour some of the original solution into a test-tube, add an equal volume of alcohol and then one drop (not more) of solution of potassium hydrate; stir the mixture with a glass rod, and shake it briskly. If a crystalline precipitate forms, especially along the lines where the glass rod touched the sides of the tube, a tartrate is certainly present.

- 4 Test for an oxalate. Put a little of the original solution into a test-tube, add enough solution of ammonium hydrate to make it alkaline (or until the liquid smells slightly of it), and then 2 or 3 c.c. of solution of calcium sulphate.

A No precipitate is formed. If so, no oxalate is present. Pass on to 5.

B A white precipitate is formed, which does not dissolve when some hydrogen acetate is added.

Then the solution contains an OXALATE.

To confirm this inference, put a little manganese dioxide into a test-tube, add about 1 c.c. of strong hydrogen sulphate, and then 2 or 3 drops of the original solution. If an effervescence occurs (best heard by holding the open end of the tube close to the ear), and if the gas given off is proved to be carbon dioxide by its rendering cloudy a drop of lime-water in the end of a pipette held within the tube (see p. 195 for details of the test), the presence of an oxalate is certain.

- 5 Test for an acetate. If no other radicle has been found there is reason to conclude that the solution contains an ACETATE.

To obtain positive evidence of this, add to some of the original solution (neutralised, if acid, by boiling with a little powdered chalk, and filtered) one drop (not more), taken up on a glass rod, of solution of iron perchloride. If the liquid turns red and when heated to boiling gradually deposits a reddish precipitate, the presence of an acetate is confirmed.

II.

ANALYSIS

of a substance which may contain any one of the following radicles:—CARBONATE, OXALATE, TARTRATE, FLUORIDE, CYANIDE, CHLORIDE, BROMIDE, IODIDE, ACETATE, NITRATE, CHLORATE (the other radicle being potassium, sodium, ammonium, or hydrogen).

A. The substance is a Solid.

- 1 Examine and note down its appearance, *e.g.* colour, shape, crystalline form (if any).

Powder some of it (if not already powdered) in a glass mortar, and put about as much as will lie on the broad end of a spatula into a test-tube; add about 20 c.c. of water, and warm it, occasionally shaking it, until the whole has dissolved; proceeding, meanwhile, with the experiments given in 2. When the solution is complete examine it as directed in 3.

Effect of heat on the substance.

- 2 Put a little of the solid substance into an ignition-tube (about enough to half fill the bulb), and heat it in the flame of a Bunsen's burner: at first gently, absorbing with a twisted slip of blotting-paper any water which may condense in the tube; afterwards to full redness. Observe which of the following effects takes place.

- A The substance remains unaltered, or simply fuses without giving off gas.

Then it is probably a CARBONATE, FLUORIDE, CYANIDE, CHLORIDE, BROMIDE, or IODIDE. Examine the solution as directed in 3.

- B The substance fuses without blackening, and gives off a gas.

Drop in a small splinter of charcoal (from the charred end of a match), add a little more of the substance and again heat. If the charcoal burns brightly, the gas is oxygen, and the substance is a CHLORATE or a NITRATE. Examine the solution as directed in 7.

- C The substance becomes charred, i.e. turns black, and gives off vapours which have a strong smell like burnt paper.

Then it is either an ACETATE, a TARTRATE, or an OXALATE. Examine the solution as directed in 3 and 8.

- D The substance volatilises entirely.

Then it is either HYDROGEN OXALATE or an ammonium salt. Examine the solution as directed in 3.

B. *The substance is a Liquid.*

[The same course is to be followed with a solution of a solid substance obtained in paragraph 1.]

3 Action on Sec whether it has any colour or smell (a cyanide litmus-paper would smell like essence of almonds). Then take out a drop on a clean glass rod, and place it on a bit of blue litmus-paper. If it does not change the colour of the litmus, put another drop on reddened litmus-paper.

A The liquid does not alter (or only alters slightly) either litmus-paper.

Then it contains a neutral salt. Pass on to 5.

B The substance reddens blue litmus-paper strongly.

Then it is probably a hydrogen salt, i.e. an acid. Pass on to 5.

C The liquid turns reddened litmus-paper strongly blue.

Then it is probably a CARBONATE or a CYANIDE. Pass on to the next paragraph (4).

Test for a carbonate.

4 Pour about 5 c.c. of the solution into a test-tube and add several drops of dilute hydrogen sulphate.

A There is little or no effervescence. If so, the substance cannot be a carbonate. Pass on to 5, in which a cyanide will be tested for.

B A strong effervescence occurs.

Then the substance most probably is a CARBONATE.

This inference is confirmed if the gas evolved is proved to be carbon-dioxide.

To make sure of this, dip the lower end of a pipette into lime-water; withdraw it so as to retain a single drop of the liquid in the contracted portion; introduce it into the test-tube in which the gas is being evolved, and gently suck a very little of the gas through the drop of lime-water. If the lime-water becomes cloudy (best judged of by holding the pipette up to the light) the presence of a carbonate is confirmed.

Tests for a bromide, iodide, chloride, or cyanide.

5 Put 3 or 4 drops of the original solution into a test-tube, add 4 or 5 c.c. of water and about half as much dilute hydrogen

nitrate; then add two drops of solution of silver nitrate. Observe whether any precipitate is formed or not.

A No precipitate is formed. If so, neither a bromide, iodide, chloride, nor cyanide can be present. Pass on to 7.

B A white or light yellow precipitate is formed.

Then the substance is a BROMIDE, IODIDE, CHLORIDE, or CYANIDE.

To find out which of them is present, proceed as follows:—

6 Tests for an iodide. Add to a portion of the original solution two and bromide. or three drops of solution of chlorine.

A The liquid turns yellow.

A BROMIDE or IODIDE is present.

Pour off one half of the yellow liquid into another tube, and add some freshly made solution of starch.

(a) *The solution turns deep blue.* An IODIDE is present (no confirmatory test is needed).

(β) *The solution remains unaltered.* A BROMIDE is present. Confirm this by adding to the rest of the yellow liquid (containing chlorine) about 1 c.c. of carbon disulphide, and shaking it up. If the globule of carbon disulphide which settles to the bottom is orange-coloured, the presence of a BROMIDE is certain.

B The liquid does not turn yellow, even on addition of a little more chlorine.

The substance present must be a CHLORIDE or a CYANIDE.

Tests for a To distinguish between them, put a little manganese chloride and manganese dioxide into a test-tube, add about 2 c.c. of cyanide. strong hydrogen sulphate, and then 6 or 8 drops of the original solution and warm gently (but do not boil the liquid).

(a) *A greenish gas is given off which has the smell of chlorine, and bleaches a strip of moist litmus-paper held in the tube.*

The substance is a CHLORIDE.

(β) *No gas having the characters of chlorine is evolved.*

The substance is a CYANIDE. (If so, the smell of hydrogen cyanide may be perceptible in the tube.)

To confirm this, add to some of the original solution, first 6 or 8 drops of solution of potassium hydrate, and then 2 or 3 drops of solution of iron protosulphate, when a greenish precipitate will form. Shake the whole thoroughly for a few seconds, and warm it gently; then add 2 or 3 c.c. of dilute hydrogen chloride. If a deep blue precipitate remains undissolved, the presence of a cyanide is certain.

Tests for a chlorate and nitrate.

7 Put 4 or 5 c.c. of water into a test-tube, add about half as much strong pure hydrogen sulphate, and one drop of indigo sulphate, and heat the mixture to boiling (the blue colour of the indigo should remain unaltered, see note on p. 164). Add to this a few drops of the original solution and boil again.

A The blue colour of the indigo remains unaltered. If so, neither a nitrate nor a chlorate is present. Pass on to 8.

B The blue colour of the indigo disappears.

The salt is a CHLORATE or a NITRATE.

To decide which is present, put 5 or 6 drops of the original solution (or a small piece of the solid substance) into a test-tube, and add about 3 c.c. of strong hydrogen sulphate.

(a) *The liquid turns yellow, and gives off a yellow gas, when warmed, which smells like a chlorine oxide.*

The substance is a CHLORATE.

(β) *The liquid does not turn yellow.*

The substance is a NITRATE.

Allow the liquid to become quite cold; then, holding the tube slanting, pour gently down the side, from a pipette, some solution of iron protosulphate, and let the liquid stand for a few minutes. If a brown ring is formed between the two liquids a nitrate is present.

Tests for a tartrate, oxalate, acetate, and fluoride.

8 Test for a tartrate. Put about 6 or 8 drops of the original solution into a test-tube, add about 5 c.c. of water and then enough solution of sodium carbonate to make it alkaline to test-paper: then add 2 or 3 drops of solution of silver nitrate (which will produce a white precipitate) and boil the liquid, adding more silver nitrate if the precipitate re-dissolves.

A The precipitate remains unaltered in colour, or only turns light brown. If so, no tartrate is present. Pass on to 9.

B The precipitate turns deep black on boiling.

Then the substance is a TARTRATE.

To confirm this, mix 4 or 5 c.c. of the original solution with an equal volume of alcohol, add one drop (not more) of solution of potassium hydrate, stir the mixture with a glass rod, and shake it briskly. If a crystalline precipitate forms more or less quickly, especially along the lines where the glass rod touched the sides of the tube, a tartrate is certainly present.

- 9 Test for an oxalate. Put a little manganese dioxide into a test-tube, add about 1 c.c. of strong hydrogen sulphate, and shake together: then add a few drops of the original solution. Observe whether any effervescence occurs (best recognised by a hissing sound when the tube is held to the ear).

A No evolution of gas occurs. If so, no oxalate is present. Pass on to 10.

- B Carbon dioxide is given off with effervescence.

(Prove that the gas is really carbon dioxide by the lime-water test, 4 B.)

The salt is an OXALATE.

To confirm this, test a little of the original solution, made alkaline by addition of ammonium hydrate, with solution of calcium sulphate. If a white precipitate is formed, insoluble on addition of hydrogen acetate, an oxalate is certainly present.

- 10 Test for an acetate. Add to some of the original solution (neutralised, if acid, by boiling with a little powdered chalk or marble, and filtered) one drop (not more), taken up on a glass rod, of solution of iron perchloride, and heat the mixture to boiling.

A No change of colour or precipitate occurs. If so, no acetate is present. Pass on to 11.

- B The liquid turns red, and when boiled gives a reddish precipitate.

The salt is an ACETATE.

To confirm this, pour about 2 c.c. of the original solution into a test-tube, add about 1 c.c. of pure alcohol, and 1 c.c. of strong hydrogen sulphate, and warm the mixture. If vapours are given off which have the fragrant smell of acetic ether, an acetate is present.

- 11 Test for a fluoride. Pour a little of the original solution into a leaden cup and evaporate it to dryness. (If the original substance was a solid, some of this may be taken.) While the evaporation is going on, cover a glass plate with wax (p. 265), and trace some letters on it with a pointed piece of wood. Pour a few drops (not more) of strong hydrogen sulphate on the residue in the cup: place over it the glass plate with the wax downwards, and warm gently for 5 minutes, taking care not to melt the wax.

If the lines are etched in the glass, the substance is a FLUORIDE.

APPENDIX D.

I.

LAWS OF CHEMICAL COMBINATION.

IT was only at the end of the last century that chemists, by accurate experiments and constant use of the balance, were enabled to establish certain laws which express the proportions by weight in which substances combine with, and act on, each other.

They are the following,—

I. LAW OF CONSTANT PROPORTION.

A particular compound always consists of the same elements united in the same proportion.

Thus water, whether obtained from wells, or the clouds, or the sea, or formed in the laboratory in the course of experiments, invariably consists of the two elements, oxygen and hydrogen, united in the proportion of 16 parts by weight of oxygen to 2 parts by weight of hydrogen. If we endeavour to form water by combining oxygen and hydrogen in any other proportions, we find that the excess of one or the other remains uncombined.

Similarly, ammonia, whether formed in nature, or obtained by decomposing wool, silk, coal, ammonium, chloride, &c., invariably contains nitrogen and hydrogen, united in the proportion of 14 parts by weight of nitrogen to 3 of hydrogen.

Two results follow from this law.

1. A few really well-made experiments are sufficient to settle once for all the composition of a substance.

If a substance is brought to a chemist, which has all the properties of water, he can feel sure what its composition is without taking the trouble actually to analyse it.

2. Any substance which is not quite constant in composition, is certainly not a chemical compound, but only a mixture. For

example, one reason for considering air to be a mixture is that the proportion of oxygen in it is slightly variable.

II. LAW OF MULTIPLE PROPORTION.

When one body combines with another in more than one proportion, the higher proportions are multiples of the lowest.

A good example of this law is afforded by the series of compounds of nitrogen with oxygen, of which a list is subjoined.

Compounds of Nitrogen with Oxygen.

Name	Composition by weight.	
	Nitrogen.	Oxygen.
Nitrogen Pentoxide	28	: 80
„ Tetraoxide	28	: 64
„ Trioxide	28	: 48
„ Dioxide	28	: 32
„ Monoxide	28	: 16

If we examine what quantity of oxygen is combined with the same quantity of nitrogen, say 28 parts, in each of the above compounds, we find that in the compound which contains least oxygen it is 16 parts: in the next, 32 parts, or twice 16; in the next, 48 parts, or three times sixteen, and so on.

Two results follow from this law.

1. We can predict the composition of compounds which have not yet been formed. Thus, if a nitrogen oxide is ever discovered which contains rather more oxygen than the pentoxide (nitrogen 28: oxygen 80), we may say with certainty that it will be composed of 28 parts of nitrogen united with $(80 + 16 =)$ 96 parts of oxygen.

2. If any substance is found to contain nitrogen and oxygen not in the proportion of 28 to 16 or a multiple of 16, we can say with certainty that it is not a chemical compound but a mixture.

Thus air contains nitrogen and oxygen, but the proportion of nitrogen to oxygen is as 28 : 8.36, which is not a simple multiple of 16. This is another reason for considering air to be a mixture.

III. LAW OF RECIPROCAL PROPORTION.

If two bodies, A and B, each combine with a third body, C, they can only combine with each other in proportions which are measures or multiples of the proportions in which they each combine with C.

Thus, nitrogen and hydrogen each combine with oxygen, in the proportions shown below.

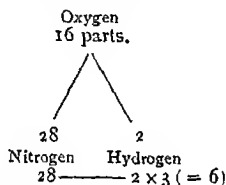
Nitrogen Monoxide	Nitrogen.	Oxygen.
	28	16
Water	Hydrogen.	
	2	16

Now, nitrogen and hydrogen combine with each other in the proportion shown below.

Ammonia	Nitrogen.	Hydrogen.
	18	6

in which we notice that 6 is an exact multiple of 2.

The following diagram may make the matter plainer.



This law extends the principle of Law II to a third body.

Thus, suppose we wish to form for the first time a combination of two substances which both form well-defined compounds with a third: then, by applying this law, we can gain a fair idea of the weights which must be taken of each to form the new compound.

Again, if, on analysing a substance, its ingredients are found not to be present in the proportions which their known combinations with other things would indicate, we may safely infer that the substance is a mixture of more than one compound.

IV. LAW OF COMPOUND PROPORTION.

The proportion in which a compound unites with anything else is the sum or a multiple of the sum of the proportions in which its elements are present in it.

Thus, taking two compounds, ammonia and hydrogen nitrate, the proportions by weight in which their elements are present in them are the following:

Ammonia.		Hydrogen nitrate.	
Hydrogen	3 parts	Hydrogen	1 part
Nitrogen	14 "	Nitrogen	14 "
	<u>7</u> "	Oxygen	48 "
Sum	= 17 "	Sum	= 63 "

Now it is found that ammonia only unites with hydrogen nitrate in the proportion of 17 parts of ammonia to 63 of hydrogen nitrate. If any other proportions are taken, there is found an excess of one or the other remaining uncombined.

The use of this law in practical work is obvious. By it we are enabled in most cases to weigh out beforehand the exact quantity of a substance required to combine with a given weight of another, so as to have no waste of either.

The above laws are simply the expression of facts observed in experimental work: they exist quite independently of any speculations as to their cause. But it was soon felt that there might be some peculiarity in the constitution of matter which would account for them all; and the hypothesis called 'The Atomic Theory,' first put into scientific form by Dalton, an English chemist, in 1801, has now been almost universally accepted as a true and sufficient explanation of them.

The Atomic Theory¹.

This is an account of the constitution of matter (*i. e.* the material of which things are made) which may be summarised in the following statements.

1. All kinds of matter are made up of very small distinct particles, which cannot be divided into smaller ones. These particles are called 'Atoms' (*ἄτομος*,—'that which cannot be cut').

2. The atoms of the same substance are all similar to one another and equal in weight (or, more strictly, in mass).

3. The atoms of different substances differ in properties; for example, in weight, in strength of affinity, &c.

4. The relative weights of these atoms are expressed by the 'smallest combining proportions' referred to in the Laws of Chemical Combination.

Thus, the number 16, by which we always *can* and generally *must* express the proportion in which oxygen combines with other things, is considered to be the weight of the atom of oxygen as compared with the weight of the atom of hydrogen, which is found to be the lightest of all atoms. In other words, the oxygen-atom is regarded as 16 times as heavy as the hydrogen-atom.

¹ A fuller account of this is given in the next section, to which this should be considered as introductory.

Similarly, the nitrogen-atom is believed to be 14 times as heavy as the hydrogen-atom, and so on for other elements; each having its own definite minimum combining proportion, which indicates the weight of its atom.

If it be asked how the relative proportions by weight in which things act on each other, as ascertained by our comparatively rough balances, can be taken to indicate the relative weights of their single atoms, which are far too small for us to weigh, the reply would be, that it is reasonable to suppose that in the large masses of atoms which we deal with in ordinary practice, each atom of the mass is acting and being acted on similarly to the rest: just as in a regiment, when marching, every individual moves similarly to and simultaneously with every other. We can hardly imagine, for example, when we mix a quantity of oxygen weighing 16 grms. with a quantity of hydrogen weighing 2 grms. and make them combine, that some of the atoms in each are affected and not others. We have every ground for believing that any chemical action between masses represents accurately the action which is going on between the individual atoms of the masses.

Now, if we allow that these atoms exist, and that all chemical changes consist in the shifting of them, like pieces on a chess-board, from one position to another, or from one group to another, all the observed facts of chemical combination summarised in the above Laws can readily be explained.

I. The 1st Law would be a necessary consequence, because if the atoms of each kind of matter have definite unalterable properties, different from those of the atoms of other kinds, then, whenever we find two or more specimens of matter having absolutely the same properties, they must be composed of the same number of atoms of the same kind, united in the same way.

II. The 2nd Law follows, because in forming compounds containing larger proportions of a given element we must add a whole atom at a time (and not half an atom or one-and-a-half atoms, since the atom is not divisible).

Thus if the smallest quantity of nitrogen monoxide contains a single atom of oxygen weighing 16 hydrogen-atoms, we must add another whole atom, also weighing 16 hydrogen-atoms, to make the dioxide. Hence nitrogen dioxide will contain twice the weight of oxygen contained in the monoxide. Similarly nitrogen trioxide will contain three times the weight, and so on.

III. The 3rd Law follows, because the atom is unalterable in weight, whatever may be the compound it exists in; and therefore when an element unites with any other substance it must do so in the proportion which the weight of its atom indicates; or in some multiple of that proportion, if more than one atom of it combines.

Thus if the weights of the atoms of hydrogen, nitrogen and oxygen are 1, 14, and 16 respectively, all their compounds, nitrogen monoxide, water, ammonia, &c. &c., must contain them in these proportions, or multiples of these proportions.

IV. The 4th Law also follows from the unalterability in weight of atoms. The weight of the smallest particle of a compound which takes part in a chemical change is as certainly the sum of the weights of the atoms which compose it, as the weight of a bag of shot is the sum of the weights of the individual shot in it.

CHEMICAL SYMBOLS.

Chemists have agreed to represent the atoms of substances by symbols; the first letter of the name of the element being generally taken to express its atom.

Thus, the atom of Oxygen is denoted by O.
" Hydrogen " H.
" Nitrogen " N.
" Carbon " C.

These symbols, therefore, represent definite weights of the respective elements, *viz.* the weight of the smallest particle of the element which can take part in a chemical action.

Thus,

H represents the unit of atomic weight, *i. e.* the weight of the hydrogen-atom, whatever that may be¹.

O represents a weight of oxygen = 16 hydrogen-atoms.

N " " " nitrogen = 14 " "

C " " " carbon = 12 " "

The smallest particle of a substance which can exist by itself and uncombined is called its 'Molecule'; and we can express the molecule of a compound by simply putting together the symbols of the atoms which compose it, just as we form a word by putting letters together. This group of symbols is called a 'Formula.'

Thus the molecule of water contains 1 atom of oxygen and 2 atoms of hydrogen, and may therefore be expressed by the formula

¹ It is probably about $\frac{1}{40,000,000,000,000,000,000}$ of a gramme.

HHO . When, however, several similar atoms are present the symbol is only written once, and a small numeral is put on the right of it and a little below, to show how many atoms are present.

Thus the usual formula for the molecule of water is H_2O .

When several molecules are to be expressed, a numeral is attached to the formula on the left-hand (in the same position, in fact, as a coefficient in algebra).

Thus the expression for 'three molecules of water' is $3\text{H}_2\text{O}$.

On the above principle the formulae of the molecules of some of the substances already examined should be written out from the following data as to their composition.

Substance.	Composition.	Formula of molecule.
Ammonia	Hydrogen Nitrogen 3 atoms. 1 atom.	
Hydrogen Nitrate ...	Hydrogen Nitrogen Oxygen 1 atom. 1 atom. 3 atoms.	
Potassium Nitrate ...	Potassium Nitrogen Oxygen 1 atom. 1 atom. 3 atoms.	
Ammonium Nitrate .	Hydrogen Nitrogen Oxygen 4 atoms. 2 atoms. 3 atoms.	
Or (to show that it contains the AMMONIUM and NITRATE radicles) ...	(Hyd. Nit.) (Nit. Oxy.) 4 at. 1 at. 1 at. 3 at.	
Nitrogen Pentoxide ...	Nitrogen Oxygen 2 atoms. 5 atoms.	
" Tetroxide ...	2 atoms. 4 atoms.	
" Trioxide	2 atoms. 3 atoms.	
" Dioxide	2 atoms. 2 atoms.	
" Monoxide ...	2 atoms. 1 atom.	

H. G. M.

II.

ON CHEMICAL SYMBOLS.

The aim of these Exercises has been to present some of the facts of chemistry without entering upon questions of chemical theory. But symbols having been used to express the principal chemical changes which form the subject of the Exercises, and the nature and strength of the various reagent solutions, a statement of the meaning of such symbols is subjoined, together with a Table of Atomic Weights.

In the beginning of Part II is an explanation of the term 'single substance.' • A chemical change consists in the conversion of any quantity of one or more single substances into an equal quantity, by weight, of one or more different single substances. The remembrance of some of the most important facts relating to these changes is facilitated by the adoption of the following hypothesis.

- It may be the case that a portion, a gramme for instance, of any single substance is an aggregate of a vast but finite number of little particles, each of which has exactly the same properties as any other and as the whole mass. These little particles are, in almost all cases, themselves divisible; but when they are divided, it is not into smaller portions of the same substance, but into distinct parts which are called atoms, as being incapable of further division. These atoms unite into fresh groups which are the molecules of substances different from the original substance; and it is in this way, according to the hypothesis, that a chemical change takes place.

A molecule may consist of any number of atoms, from one up to a very large number. The molecules of the elements are supposed to consist either of single atoms or of two or more similar atoms united together. Differences in the properties of different substances may be due to the differences in the nature, or number, or arrangement, of the atoms of which their molecules consist.

The weight of a molecule is the sum of the weights of its atoms; and, since different atoms have very different weights, and different molecules consist of very different numbers of atoms, the weight of one molecule may be several hundred times as great as that of another.

Chemists have agreed to represent the various atoms by letters, that assigned to each being generally the initial letter of the name of that element whose molecule is made up of such atoms. Thus H represents the hydrogen-atom and O the oxygen-atom. But as the names of several elements have the same initial letter, the requisite variety has been obtained by taking the Latin instead of the English name, or by using two letters. Thus K represents the potassium-atom (Kalium), Co the cobalt-atom, Sb the antimony-atom (Stibium). The union of two or more atoms to form a molecule or group of atoms is represented by placing their symbols together, thus CoO represents a molecule of cobalt oxide which consists of a cobalt-atom united to an oxygen-atom. When similar atoms are united, a numeral is affixed to the symbol of the atom, to

represent its repetition so many times; thus, the molecule of water is expressed by H_2O instead of HHO .

It will be plain that, according to the hypothesis stated above, the atoms are not actual portions of any known substance except in the case of those substances whose molecules consist of single atoms, where, consequently, the atom is also a molecule. The smallest particle, or molecule, of common salt is represented by the formula $NaCl$: its atoms Na and Cl can be transferred to other molecules, but cannot be obtained as distinct substances; we know them only as constituents of a number of different molecules. And in the same way the molecule of hydrogen is represented by H_2 , the letter H representing, not a minute portion of hydrogen, but a constituent of hydrogen, a hydrogen-atom, a portion of matter weighing half as much as the smallest particle of hydrogen which is transferable in chemical changes from one molecule to another.

The determination of the relative weights of different atoms depends upon (1) the accurate quantitative analysis of a number of single substances, (2) a decision as to the constitution of the molecules of these substances. For example, analysis shows that nine weights of water can be decomposed into eight weights of oxygen and one weight of hydrogen. Choosing the weight of the hydrogen atom, as being the smallest relative weight we have to do with, as the unit of our system, if we decide that a molecule of water consists of one hydrogen-atom combined with one oxygen-atom, the weight of the oxygen-atom must be 8. If we decide that a molecule of water consists of one hydrogen-atom combined with two oxygen-atoms, we must take 4 to be the atomic weight of oxygen; or if we have reason, as in fact we have, to regard the molecule of water as consisting of two hydrogen-atoms and one oxygen-atom, we must call the weight of the oxygen-atom 16.

The reasons which guide us in deciding what is the constitution of the molecule of a substance may be stated summarily under two heads: (1) that constitution is most probably true which affords the simplest account of the changes which the molecule is known to undergo, and which best exhibits the analogy between the substance in question and other substances which it resembles; (2) that constitution is most probably true which makes the molecular weight of the substance bear to the molecular weights of other substances the same ratio which its vapour-density bears to theirs. As this latter guide to the molecular constitution of substances is only available in the case of substances which can be volatilized without

decomposition at a moderate heat, the weights of those atoms have been most definitely fixed which enter into the molecules of such substances.

It has also been observed that the relative weights of the atoms are in most cases nearly in inverse proportion to the specific heats of the elements which they form. This observation furnishes us with another criterion of the true atomic weight.

The following Table of Atomic Weights has been arrived at in the manner indicated.

TABLE OF ATOMIC WEIGHTS.

H	represents a	Hydrogen-atom weighing	1
Li	"	Lithium-atom	7
B	"	Boron-atom	11
C	"	Carbon-atom	12
N	"	Nitrogen-atom	14
O	"	Oxygen-atom	16
F	"	Fluorine-atom	19
Na	"	Sodium-atom	23
Mg	"	Magnesium-atom	24
Al	"	Aluminium-atom	27.5
Si	"	Silicon-atom	28
P	"	Phosphorus-atom	31
S	"	Sulphur-atom	32
Cl	"	Chlorine-atom	35.5
K	"	Potassium-atom	39
Ca	"	Calcium-atom	40
Ti	"	Titanium-atom	50
V	"	Vanadium-atom	51.2
Cr	"	Chromium-atom	52.5
Mn	"	Manganese-atom	55
Fe	"	Iron-atom	56
Co	"	Cobalt-atom	59
Ni	"	Nickel-atom	59
Cu	"	Copper-atom	63.5
Zn	"	Zinc-atom	65
As	"	Arsenic-atom	75
Se	"	Selenium-atom	79
Br	"	Bromine-atom	80
Sr	"	Strontium-atom	87.5
Mo	"	Molybdenum-atom	92
Pd	"	Palladium-atom	106.5
Ag	"	Silver-atom	108
Cd	"	Cadmium-atom	112
Sn	"	Tin-atom	118
U	"	Uranium-atom	120
Sb	"	Antimony-atom	122
I	"	Iodine-atom	127
Ba	"	Barium-atom	137

W	represents a	Tungsten-atom	weighing	184
Au	"	Gold-atom	"	196.7
Pt	"	Platinum-atom	"	197
Hg	"	Mercury-atom	"	200
Tl	"	Thallium-atom	"	204
Pb	"	Lead-atom	"	207
Bi	"	Bismuth-atom	"	210

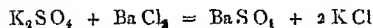
This Table, which includes all the atoms which are not of very rare occurrence, enables us to calculate the weight of any molecule whose formula is known to us, relatively to the weight of a hydrogen-atom which is assumed as the unit. Thus, the formula of calcium carbonate being CaCO_3 , the weight of its molecule is $(40 + 12 + (3 \times 16) = 100$; that is to say, a molecule of calcium carbonate weighs a hundred times as much as a hydrogen-atom.

A Table of Molecular Weights, which might be extended to all substances whose constitution has been determined, would have the following form.

H_2	represents a molecule, or 2 parts by weight, or 1 volume of Hydrogen.
N_2	" " 28 " " Nitrogen.
Hg	" " 200 " " Mercury.
P_4	" " 124 " " Phosphorus.
NH_3	" " 17 " " Ammonia.
C_2H_4	" " 28 " " Ethylene.
&c. &c.	

In the equations by which chemical changes are represented, the sign = has not simply its algebraic sense of 'equals,' but should rather be read 'is converted into.' That the substances formed in a chemical change weigh as much as the substances that went to form them, is a fact which renders the symbol appropriate, but is not all that it is understood to mean. The sign +, connecting the symbols of two molecules, denotes that these molecules disappear, or are formed, simultaneously; it may be expressed in reading by the word 'and.'

Thus the equation



should be read thus, 'a molecule of potassium sulphate and a molecule of barium chloride are converted into a molecule of barium sulphate and two molecules of potassium chloride.' To obtain the relations by weight between the different substances we write down

$\text{K}_2 - 78$	$\text{Ba} - 137$	$\text{Ba} - 137$	$\text{K} - 39$
$\text{S} - 32$	$\text{Cl}_2 - 71$	$\text{S} - 32$	$\text{Cl} - 35.5$
$\text{O}_4 - 64$		$\text{O}_4 - 64$	
$\text{K}_2\text{SO}_4 - 174$	$\text{BaCl}_2 - 208$	$\text{BaSO}_4 - 233$	$\text{KCl} - 74.5$

hence we see that 174 weights of potassium sulphate and 208 weights of barium chloride are converted into 233 weights of barium sulphate and 149 weights of potassium chloride.

Since equal volumes of all gases contain, under the same conditions, the same number of molecules, equations representing changes in which gases take part may be read off at once as expressing changes of volume. The common volume occupied by an equal number of molecules of the different kinds of matter in the gaseous state should be called one volume.

Thus, $2 \text{ C O} + \text{O}_2 = 2 \text{ C O}_2$ may be read 'two volumes of carbon protoxide and one volume of oxygen are converted into two volumes of carbon dioxide.' If in comparing the molecular weights and volumes of different substances we take a gramme for unit instead of the weight of an atom of hydrogen, the common volume occupied by 28 grms. of carbon protoxide, 32 grms. of oxygen, 44 grms. of carbon dioxide, &c. is 22.3 litres.

A. V. H.

APPENDIX E.

I.

TABLES OF MEASURES AND WEIGHTS.

The system of measures and weights used in this book is that which is known as the metric system.

The unit of the system is the **METRE**, the length of which is $\frac{1}{40,000,000}$ th part of the earth's circumference, as determined in 1796 by Delambre and others.

1. Length.

In deriving other measures of length from the metre, only the number 10 and its multiples are employed; and names are selected which denote the relation of the particular measure to the unit.

Thus, the next larger measure is a length ten times that of the metre, and is called a **decametre** (Gr. *δέκα*, *deca*, ten). The next larger measure is a length 100 (that is, 10×10) times that of the metre, called a **hectometre** (Gr. *ἑκατον*, *hecaton*, a hundred). The largest measure practically used, is a length of 1000 (that is, $10 \times 10 \times 10$) metres, called a **kilometre** (Gr. *χίλια*, *chilia*, a thousand).

Similarly, for the smaller measures, we have a length of $\frac{1}{10}$ of a metre, called a **decimetre** (Lat. *decem*, ten); a length of $\frac{1}{100}$ of a metre, called a **centimetre** (Lat. *centum*, a hundred); and a length of $\frac{1}{1000}$ of a metre, called a **millimetre** (Lat. *mille*, a thousand).

Thus, the names of all the measures larger than the unit, are constructed by adding to the name of the unit a prefix derived from a *Greek* numeral; the names of the measures smaller than the unit, are obtained by adding to the name of the unit a prefix derived from a *Latin* numeral.

A complete table of the measures of length, and their value in English measure, is given below, and



Fig. 116.

Fig. 116 shows the actual length of a decimetre, which is divided into centimetres and millimetres; a scale of English inches is added for comparison, by which it is seen that a decimetre is very nearly equal to four inches.

TABLE OF THE MEASURES OF LENGTH.

(The usual abbreviations are put in brackets.)

Kilometre	=	1000 metres	=	1093.6 yards	=	0.6214 of a mile.
Hectometre	=	100 "	=	3937.08 inches	=	109.36 yards.
Decametre	=	10 "	=	393.71 "	=	10.93 "
Metre (m.)	=	1 metre	=	39.37 "	=	1.09 "
Decimetre	=	0.1 "	=	3.94 "		
Centimetre (cm.)	=	0.01 "	=	0.39 "		
Millimetre (mm.)	=	0.001 "	=	0.039 "		

The table may also be put in the following form:—

10 millimetres	=	1 centimetre.
10 centimetres	=	1 decimetre.
10 decimetres	=	1 metre.
10 metres	=	1 decametre.
10 decametres	=	1 hectometre.
10 hectometres	=	1 kilometre.

2. Volume.

The unit of volume is a cube, each of the sides of which measures one decimetre, in other words, it is 'one cubic decimetre.' It is called a 'litre,' and from it the other measures of volume are derived by taking $\frac{1}{10}$, $\frac{1}{100}$, and $\frac{1}{1000}$ of its size for the smaller ones, and 10 times, 100 times, and 1,000 times its size for the larger ones, precisely as those of length are derived from the metre. Their names also are formed on the same principle, by adding to the word '*litre*' prefixes derived from the Latin for the smaller measures, and prefixes derived from the Greek for the larger ones.

TABLE OF THE MEASURES OF VOLUME.

Kilolitre	=	1000 litres	=	220.01 gallons.
Hectolitre	=	100 "	=	22.00 "
Decalitre	=	10 "	=	2.20 "
Litre	=	1 "	=	1.76 pints.
Decilitre	=	100 c.c.	=	0.1 "
Centilitre	=	10 c.c.	=	0.01 "
Millilitre	=	1 c.c.	=	0.001 "

(or cubic centimetre)

It should be noted,

1. That the name 'cubic centimetre' is almost universally used instead of 'millilitre' (a cubic centimetre being readily demonstrated to be one-thousandth of a cubic decimetre or litre).

2¹. That quantities smaller than the litre are usually expressed in cubic centimetres (instead of decilitres, &c.). Thus half a litre would be expressed (not as 5 decilitres but) as '500 c.c.'; and three-fourths of a litre would be expressed (not as 7 decilitres 5 centilitres but) as '750 c.c.'

3. Weight.

The unit of weight (or, more strictly, of mass) is the weight of 1 cubic centimetre of water at the temperature of 4° Centigrade¹. It is called a 'gramme,' and the other weights are multiples and subdivisions of it, derived in the same way and named on the same principle as above explained.

TABLE OF THE MEASURES OF WEIGHT.

Kilogramme	= 1000 grammes	= 2.205 lbs. (avoird.)
Hectogramme	= 100 "	= 3.527 oz. "
Decigramme	= 10 "	= 0.35 oz. "
Gramme	= 1 "	= 15.43 grains.
Decigramme	= 0.1 "	= 1.54 "
Centigramme	= 0.01 "	= 0.154 "
Milligramme	= 0.001 "	= 0.015 "

4. Area.

A series of measures of surface or area is sometimes used, of which the unit is the 'are,' which is a surface 1 decametre square.

The hectare is very nearly 2½ acres.

RULES FOR REDUCTION.

(These apply to all the tables given above.)

I. To reduce the larger and smaller measures to the unit, and vice versa. (Principle.—*The name of each measure expresses what multiple of the unit it is.*)

A. To reduce a given larger measure to the unit, or a given unit to one of the smaller measures.

Multiply by the number expressed in the name of the measure.

Examples:

Reduce 18 kilometres to metres. $18 \times 1000 = 18,000$ m.

Reduce 6 grammes to centigrammes. $6 \times 100 = 600$ centigrammes.

¹ The reason why this particular temperature is specified in defining the gramme is as follows: A given mass of water alters in bulk as its temperature changes (as is more fully explained in treatises on Heat); but at 4° C. it occupies the smallest space that it ever occupies while in the liquid state. Hence a cubic centimetre of water has more matter in it, and therefore weighs more, at 4° C. than at any other temperature.

B. To reduce a given smaller measure to the unit, or a given unit to one of the larger measures.

Divide by the number expressed in the name of the measure.

Examples :

Reduce 1885 centimetres to metres. $1885 \div 100 = 18.85$ m.

Reduce 1724 litres to decalitres. $1724 \div 10 = 172.4$ decalitres.

M. To reduce any given measure to the next larger or the next smaller measure. (Principle. — *Each measure is ten times the next smaller one, and one-tenth of the next larger one.*)

A. To reduce a measure to the next larger one.

Divide the number by 10.

Example : Reduce 152 centigrammes to decigrammes.

$$152 \div 10 = 15.2 \text{ decigrammes.}$$

B. To reduce a measure to the next smaller one.

Multiply the number by 10.

Example : Reduce 16.2 kilometres to hectometres.

$$16.2 \times 10 = 162 \text{ hectometres.}$$

It is obvious that, since our system of numeration is, like the metric system itself, a *decimal* system, *i. e.* is based on the number 10, all the processes of multiplication and division required by the above rules are extremely simple. The actual figures have not to be changed at all; their value is altered simply by changing their place in reference to the units-figure. This is, of course, done by altering the position of the decimal point; the latter being always considered to exist, even if not actually expressed, immediately after (that is, to the *right* of) the units-figure.

Similarly, decimal fractions of the measures may always be read off into their equivalents without altering the figures, by simply attending to the value of each figure as fixed by the position of the decimal point. Thus

$$\begin{aligned} 1.887 \text{ metre} &= 1 \text{ metre} + .8 \text{ metre} + .08 \text{ metre} + .007 \text{ metre.} \\ &= 1 \text{ metre, } 8 \text{ decimetres, } 8 \text{ centimetres, } 7 \text{ millimetres.} \end{aligned}$$

TABLES OF ENGLISH MEASURES.

1. Length.

1	inch	=	2.54	centimetres.
12	inches	= 1 foot	=	30.48 "
3	feet	= 1 yard	=	91.44 "
5½	yards	= 1 pole	=	5.03 metres.
4	poles	= 1 chain	=	20.12 "
40	poles	= 1 furlong	=	201.16 "
8	furlongs	= 1 mile	=	1609.3 "

2. Volume.

1 cubic inch	=	16.38 cubic centimetres.
1728 cubic inches	= 1 cubic foot	= 28.31 litres.
61.027 "	= 1 litre.	
1 drachm	= 0.216 cubic inch	= 3.55 cubic centimetres.
8 drachms	= 1 ounce	= 28.4 " "
20 ounces	= 1 pint	= 567.9 " "
2 pints	= 1 quart	= 1.136 litres.
4 quarts	= 1 gallon	= 4.544 "
1 gallon	= 277.274 cubic inches	= 70,000 grains (or 10 lbs avoird.) of
	distilled water at the temperature of 60° F. (15.5° C.).	0

3. Weight.

(a) *Apothecaries.*

1 gram	=	0.0648 gramme.
20 grains	= 1 scruple	= 1.296 "
3 scruples	= 1 drachm	= 3.888 "
8 drachms	= 1 ounce	= 31.104 "
12 ounces	= 1 pound	= 373.248 "

(b) *Avoirdupois.*

1 grain	=	0.0648 gramme.
27.34 grains	= 1 drachm	= 1.772 "
16 drachms	= 1 ounce	= 28.35 "
16 ounces	= 1 pound	= 453.6 "
112 pounds	= 1 cwt.	= 50.8 kilogrammes.

II.

THERMOMETRIC SCALES.

The temperatures mentioned in this book are all expressed on the Centigrade scale.

According to this scale, the space through which the column of mercury in a thermometer moves, when passing from the temperature at which water freezes to the temperature at which water boils (under a pressure equal to that of a column of mercury 760 mm. high), is divided into 100 equal parts or degrees, and the scale is extended below the freezing-point and above the boiling-point of water, in divisions of the same value.

The point at which the mercury column stands when the thermometer is immersed in melting ice is marked 0°, and the degrees

Below this point are distinguished by a *minus* sign, thus $+1^{\circ}$, -2° , &c.

The point at which the mercury column stands when the thermometer is immersed in the steam from boiling water (the barometric column being 760 mm.) is marked 100° .

In the Fahrenheit scale, which is not yet superseded in this country, the space between the freezing-point and the boiling-point of water is divided into 180 degrees, and, moreover, the freezing-point of water is marked 32° instead of 0° , the boiling-point of water being consequently marked 212° instead of 180° .

The points to be borne in mind, then, in converting temperatures expressed on the one scale to the corresponding temperatures on the other scale, are—

1. The same space is divided on the Centigrade scale into 100 parts, on the Fahrenheit scale into 180 parts.

Consequently, 1 degree on the Centigrade scale is equal in length to $(\frac{100}{180}) = \frac{5}{9}$ of a degree on the Fahrenheit scale; and 1 degree on the Fahrenheit scale is equal in length to $(\frac{180}{100}) = \frac{9}{5}$ of a degree on the Centigrade scale.

$$\begin{aligned} \text{For since } 100^{\circ} \text{ C.} &= 180^{\circ} \text{ F.} \\ 100^{\circ} \text{ C.} &: 180^{\circ} \text{ F.} :: 1^{\circ} \text{ C.} : \frac{9}{5}^{\circ} \text{ F.} \\ \text{and } 180^{\circ} \text{ F.} &: 100^{\circ} \text{ C.} :: 1^{\circ} \text{ F.} : \frac{5}{9}^{\circ} \text{ C.} \end{aligned}$$

2. The point marked 0° on the Centigrade scale is marked 32° on the Fahrenheit scale.

Consequently, in order to bring the two scales to the same level, we must subtract 32 from the number of Fahrenheit degrees *before* converting them into Centigrade degrees; and, in the reverse process, *after* converting the Centigrade degrees into Fahrenheit degrees, we must add 32.

If 0° C. expressed the same temperature as 0° F. , then, clearly—

$$\begin{aligned} 1^{\circ} \text{ C.} &\text{ would } = 1.8^{\circ} \text{ F.} \\ 5^{\circ} \text{ C.} & \quad \quad = 9^{\circ} \text{ F.} \\ 10^{\circ} \text{ C.} & \quad \quad = 18^{\circ} \text{ F.} \\ \&c. \quad \quad \quad \&c. \end{aligned}$$

But 0° C. marks a point of temperature = 32° F. Hence all the above Nos. Fahr. have to be increased by 32 (if, as it were, in the row), so that

$$\begin{aligned} 1^{\circ} \text{ C.} &= (1.8 + 32) = 33.8^{\circ} \text{ F.} \\ 5^{\circ} \text{ C.} &= (9 + 32) = 41^{\circ} \text{ F.} \\ 10^{\circ} \text{ C.} &= (18 + 32) = 50^{\circ} \text{ F.} \end{aligned}$$

Similarly in reducing Fahr. to Cent. we must take away 32 from the number of degrees (thus practically lowering it in the scale) *before* applying the rule. Thus

$$59^{\circ} \text{ F.} - 32 = 27^{\circ} \parallel 27^{\circ} \times \frac{5}{9} = 15^{\circ} \text{ C.}$$

The rules, therefore, may be thus expressed :—

1. To convert Fahrenheit degrees into Centigrade degrees,
Subtract 32 from the number of degrees, and multiply the remainder by $\frac{5}{9}$ (or 0.5)¹.
2. To convert Centigrade degrees into Fahrenheit degrees,
Multiply the number of degrees by $\frac{9}{5}$ (or 1.8) and add 32 to the product².

In applying the rule to degrees low in the scale, the character of the sign + or - must be carefully attended to, and considered in its algebraic sense. Thus,—

$$\begin{array}{ll} 23^{\circ} \text{ F.} - 32 = -9^{\circ} & \parallel \quad -9^{\circ} \times \frac{5}{9} = -5^{\circ} \text{ C.} \\ -40^{\circ} \text{ F.} - 32 = -72^{\circ} & \parallel \quad -72^{\circ} \times \frac{5}{9} = -40^{\circ} \text{ C.} \end{array}$$

$$^1 n^{\circ} \text{ F.} = (n - 32) \frac{5}{9}^{\circ} \text{ C.}$$

$$^2 n^{\circ} \text{ C.} = (\frac{9}{5} n + 32)^{\circ} \text{ F.}$$

This rule may also stand as follows :—

Double the number of degrees, subtract $\frac{1}{10}$ of this product, and add 32 to the remainder.

$$\begin{array}{rcl} \text{Thus, } 25^{\circ} \text{ C.} \times 2 & = & 50 \\ 50 - 5 & = & 45 \\ 45 + 32 & = & 77^{\circ} \text{ F.} \end{array}$$

III.

TABLE OF THE SOLUBILITY OF SALTS.

This Table is intended to indicate the solubility in water and acids of the single salts formed by the union of the different radicles treated of in the foregoing pages, and has been compiled mainly upon the authority of Störer's 'Dictionary of Solubilities.'

The degrees of solubility are, however, so numerous that it is difficult or impossible to draw a sharp line between a soluble and an insoluble substance. The statements in the Table must therefore be only regarded as approximations; as relatively rather than absolutely true.

It is hardly necessary to remark that in cases where a substance is said to dissolve in an acid, the phenomenon usually consists in the formation, by the action of the acid, of a salt soluble in water.